Large spin-orbit splitting of deep in-gap defect states of engineered sulfur vacancies in monolayer WS$_2$

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Structural defects in 2D materials offer an effective way to engineer new material functionalities beyond conventional doping in semiconductors\textsuperscript{1–5}. Specifically, deep in-gap defect states of chalcogen vacancies have been associated with intriguing phenomena in monolayer transition metal dichalcogenides (TMDs)\textsuperscript{1,2,6–10}. Here, we report the direct experimental correlation of the atomic and electronic structure of a sulfur vacancy in monolayer WS\textsubscript{2} by a combination of CO-tip non-contact atomic force microscopy (nc-AFM) and scanning tunneling microscopy (STM). Sulfur vacancies, which are absent in as-grown samples, were deliberately created by annealing in vacuum. Two energetically narrow unoccupied defect states of the vacancy provide a unique fingerprint of this defect. Direct imaging of the defect orbitals by STM and state-of-the-art GW calculations reveal that the large splitting of 252 meV between these defect states is induced by spin-orbit coupling. The controllable incorporation and potential decoration of chalcogen vacancies provide a new route to tailor the optical, catalytic and magnetic properties of TMDs.

Transition metal dichalcogenides (TMDs) and other layered materials have recently attracted considerable interest because of their unique properties arising from the combination of quantum confinement, reduced screening and lack of inversion symmetry in the monolayer limit. The strong confinement, however, also causes TMD properties to be particularly sensitive to defects. Structural defects in TMDs are thought to substantially modify optoelectronic properties and induce catalytic functionality to the otherwise inert surface. Particularly, chalcogen vacancies have been attributed to a variety of phenomena including single-photon emission\textsuperscript{6}, defect-bound excitons\textsuperscript{2,7,9,10}, catalytic activity\textsuperscript{8} and hopping transport\textsuperscript{1}. In most of these studies, the chalcogen vacancy functionality was only indirectly inferred by the presence of this defect in transmission electron microscopy (TEM)\textsuperscript{1,5,11–14}. Moreover, TMD monolayers are known to be electron beam sensitive and vacancy defects can be created in-situ by knock-on or radiolysis effects\textsuperscript{1,5,11–14}, as reflected in the very high reported defect densities on the order of 10\textsuperscript{13} cm\textsuperscript{-2}, even in exfoliated samples\textsuperscript{14}, with an estimated vacancy generation rate of about 5 \times 10\textsuperscript{10} cm\textsuperscript{-2}s\textsuperscript{-1} \textsuperscript{1,11}.

A decisive factor for the functionality of defects is the creation of defect states in the
band gap of the semiconductor. While TEM can routinely resolve the atomic lattice, the
electronic structure around the Fermi level is not easily accessible by TEM. Conversely,
scanning tunneling microscopy (STM) can probe the electronic structure of even single de-
fects\textsuperscript{10,15–21}, but the defect assignment is not straightforward because their STM contrast is
dominated by their electronic states, and tip-dependent contrast inversion makes it difficult
to assign lattice sites. Both of these complications have lead to recent contradictory defect
identification in TMDs by STM\textsuperscript{10,18,21}.

In this study, we use a combination of CO-tip noncontact atomic force microscopy
(nc-AFM), scanning tunneling microscopy/spectroscopy (STM/STS) and \textit{ab initio} GW cal-
culations to unambiguously identify and characterize the chalcogen vacancy in WS\textsubscript{2}. We
find that chalcogen vacancies are largely absent in as-grown TMD samples under ambient
conditions. Chalcogen vacancies were, however, deliberately created by \textit{in vacuo} anneal-
ing at elevated temperatures. In STS, the sulfur vacancy in WS\textsubscript{2} exhibits a characteristic
fingerprint with two narrow unoccupied defect states accompanied by vibronic satellite
peaks. The observed splitting between the two defect peaks is caused by extraordinarily
strong spin-orbit coupling. Our results challenge the current perception of the presence and
functionality of the most discussed defect in TMDs. It also opens up new avenues for de-
fect engineering in the context of valleytronics, solitary dopant optoelectronics and catalysis.

The WS\textsubscript{2} samples are grown using chemical vapor deposition (CVD) on graphitized SiC
substrates as describe in the Methods section. As argued in a recent paper\textsuperscript{20}, chalcogen site
defects are abundant but they can be identified as oxygen substituents rather than chalcogen
vacancies with a radically different electronic structure\textsuperscript{20,22}. Undecorated sulfur vacancies
can, however, be readily generated by annealing or ion bombardment in vacuum as reported
previously\textsuperscript{2,11,23,24}. Calculations also showed that in vacuum, the chalcogen vacancy has the
lowest formation energy of any intrinsic defect in several TMD materials\textsuperscript{12,14}. Note that
a recent study found that this is not necessarily the case when other molecules are present\textsuperscript{20}.

In Fig. 1 STM and nc-AFM maps of a substituted oxygen defect (O\textsubscript{S}) and a sulfur vacancy
(V\textsubscript{S}) are shown in both the top and bottom sulfur layer (facing the tip or the underlying
graphene) of the monolayer WS\textsubscript{2}. At moderate annealing temperatures of around 250\textdegree C
only the O$_S$ top and bottom defects are observed along with tungsten substitutions. When the sample is annealed to 600 °C, pristine, undecorated sulfur vacancies were also detected in addition to all other point defects that were present before. Substitutional oxygen and sulfur vacancies can be clearly distinguished from each other in STM (c.f. Fig. 1a,c and Fig. 1b,d). Note that a similar STM contrast like in Fig. 1b,d that we assign to O$_S$ has been reported for MoS$_2$ and WSe$_2$ and was ascribed either to a sulfur vacancy$^{18}$ or a tungsten vacancy$^{10,21}$, revealing the difficulty of defect structure identification based on STM alone.

Our defect structure assignment is based on the CO-tip nc-AFM images that are in excellent agreement with simulations based on the probe particle model$^{25}$ (see Fig. S3) as well as the distinct defect electronic structure as discussed in detail below. While the CO-tip in nc-AFM is exceptionally sensitive to the outermost surface layer, it is difficult to distinguish between vacancies and substituted oxygens, which are located slightly below the surface sulfur plane. For both types of defects the surrounding surface sulfur atoms relax similarly and the oxygen atom of O$_S$ binds closer to the tungsten plane, the defect in the top sulfur layer appears as a missing S atom, and the defect in the bottom sulfur layer appears as a S atom that is protruding from the surface for both V$_S$ and O$_S$ (c.f. Fig. 1e,f and Fig. 1g,h). In direct comparison (i.e. when measured in the same image), O$_S$ appears slightly more attractive than V$_S$ (see Fig. S2). We would like to point out that TEM would not be able to discriminate an oxygen substituent from a chalcogen vacancy because the sulfur atom on the opposite side of the layer masks the presence of the low atomic number O atom. Electronically, however, the sulfur vacancy and the O substituent are fundamentally different. While O$_S$ does not feature defect states in the WS$_2$ band gap$^{20}$, V$_S$ does have pronounced deep in-gap defect states, which will be discussed next.

In Fig. 2a,b STS spectra of a single V$_S$ are shown. It is important to note that both the top and bottom V$_S$ are electronically equivalent, indicating the negligible influence of the graphene substrate (see Fig. S6). The defect introduces a series of sharp resonances in the unoccupied spectrum at positive sample bias and a single resonance at negative bias. The occupied defect state resonance is located about 300 meV below the valence band maximum (VBM) overlapping with delocalized bulk states, similar to the defect resonance observed for O$_S$. Strikingly, we find two unoccupied defect states at 774 meV and 522 meV
below the conduction band minimum (CBM), deep in the band gap. Each of these defect state resonances is accompanied by vibronic satellite peaks that stem from inelastically tunneling electrons commonly observed in transport spectroscopy of molecules\textsuperscript{26}. Using the Franck-Condon model we can estimate the electron-phonon coupling strength and the dominant phonon mode that is excited when transiently charging the defect by tunneling electrons. From the relative peak intensities and the vibronic peak separation we estimate a Huang-Rhys factor of HR = 1.2 with a phonon mode of $\hbar \omega = 12\text{ meV}$ for the lower energy defect state and HR = 0.7 with $\hbar \omega = 18\text{ meV}$ for the higher energy defect state. Therefore, the electron-phonon coupling strength is in the intermediate regime (HR $\approx$ 1). The initial broadening of 9 meV (full width at half maximum) increases for higher phonon replicas.

The $V_S$ defect’s purely electronic states at the lowest excitation energy are denoted zero-phonon line (ZPL) in Fig. 2b, following the conventions used in absorption/emission spectroscopy. Most notably, both defect resonances exhibit the same spatial electron distribution as evident from the dI/dV maps shown in Fig. 2c. We attribute this observation to a lifted degeneracy induced by spin-orbit coupling (SOC). Hence, the energy separation between the two elastic excitations quantifies the spin-orbit interaction as 252 meV, which is exceptionally large. As we will see below, each of the two peaks is composed of two degenerate defect states. In dI/dV maps these states are imaged as a superposition of the charge densities of the degenerate orbitals. The defect states appear different for the top and bottom $V_S$ since the defect and its orbital are not mirror-symmetric with respect to the tungsten plane.

The spectra shown in Fig. 2a,b are measured on WS\textsubscript{2}(1ML) on bilayer graphene. On a monolayer graphene substrate, the filled-state spectrum is qualitatively different. We find an additional major resonance around $-1.3\text{ V}$ and the valence band is pushed upwards (see Fig. S4). This additional feature is identified as a charging peak (see Fig. S5). The different behavior of mono- vs bilayer graphene substrate can be explained by the observed energetic shift of the $V_S$ defect states and conduction band towards lower energies of about 160 meV. The shift is induced by a combination of screening effects and shift in work function between mono- and bilayer graphene\textsuperscript{27}. Since the $V_S$ defect states shift closer to the Fermi level on the monolayer graphene substrate, tip-induced band bending is sufficient to pull the lower
the Fermi level, hence negatively charging the defect in the vicinity of the tip at sufficiently large electric fields. Using the charging peak, a field-induced shift of 11\% of the applied bias voltage was estimated at the chosen tunneling set point. Note that the defect state energies stated above were corrected for this field-induced shift. For a detailed discussion about the tip-induced charging we refer to the SI.

To verify our interpretation of the spin-orbit split defect states of the sulfur vacancy, we calculated the electronic structure of a WS₂ monolayer with chalcogen vacancy point defects using the \textit{ab initio} GW approach. We constructed a supercell consisting of 5 unit cells along each crystalline-axis direction of the monolayer plane (namely 50 S atoms and 25 W atoms) and then removed a single chalcogen atom⁴. We accounted for spin-orbit coupling via a fully-relativistic, noncollinear density functional theory (DFT) starting point as implemented in Quantum Espresso and built one-shot GW energy corrections on top of it, as implemented in the BerkeleyGW package (see Methods section for full computational details). Fig. 3 shows the resulting DFT band structures computed within the local density approximation (LDA) and GW energy levels. At both the DFT and GW level, the sulfur vacancy introduces four unoccupied in-gap states, which form two pairs of nearly-degenerate flat bands in the gap, corresponding to the two deep in-gap resonances in the dI/dV. The nearly-degenerate state are time-reversal pairs whose degeneracy has been lifted slightly due to interaction between periodic images of the 5x5 supercell. The charge distribution of the two in-gap states are highly localized around the S vacancy, as shown in Fig. 3a. The calculated defect orbitals for the top and bottom V_S are in excellent agreement with the corresponding dI/dV maps shown in Fig. 2c. In addition, an occupied doubly-degenerate defect-localized resonant state appears in the valence region, in agreement with experimental observation (black line in Fig. 3c). Fig. 3c shows the resulting energy gaps. The one-shot GW correction opens the VBM-CBM gap to 2.8 eV (compared to the calculated DFT gap of 1.6 eV), comparing well with the experimental value of 2.5 eV. The error bar of the bandgap within our calculation is estimated to be 150 meV - as a result of the sensitivity of the GW approach to the DFT starting point and to structural effects. Note that screening effects from the graphene substrate are not included in the calculations but can be expected to reduce the gap by a few hundred meV²⁸,²⁹. Importantly, the GW gap between the highest in-gap defect state and the conduction band is 0.6 eV, in reasonable agreement with the
measured value of 0.52 eV in experiment. The spin-orbit energy splitting between the two doubly-degenerate in-gap states is 180 meV from our calculations.

Our theoretical calculations also shed light on the spin-orbit splitting and character of the in-gap states. Although many theoretical studies predicted the chalcogen vacancy to form in-gap states\textsuperscript{2,12-14,19}, only a few explicitly consider the effect of SOC\textsuperscript{30,31}. We find that each in-gap peak in the d$I$/d$V$ corresponds to two degenerate states belonging to a time-reversal pair. The character of the in-gap states consists primarily of W d-states, which are responsible for the large magnitude of the spin-orbit splitting, with some smaller contributions from the S 3p and W 6p states (see SI). The lower-energy in-gap states have a larger contribution from $J = 3/2$ states, and the higher energy in-gap states have a larger contribution from $J = 5/2$ states. The close correspondence between the in-gap states in theory and experiment are a clear indication of the presence of sulfur vacancies. Importantly, the hybridization between defect-localized in-gap states and delocalized, pristine-like states can lead to significant valley depolarization\textsuperscript{4} and suggests a path to control spin-valley selectivity through defect engineering.

In summary, we created and identified individual sulfur vacancies in monolayer WS\textsubscript{2} by a combination of atomic-resolution nc-AFM, STS and \textit{ab initio} GW calculations. We show that a sulfur vacancy gives rise to two unoccupied in-gap defect states that appear as sharp resonances followed by vibronic satellite peaks in STS. The deep in-gap states act as a strong atom trap, which explains why undecorated chalcogen vacancies are largely absent in as-grown TMD samples under ambient conditions. Remarkably, the degeneracy between the four $V_S$ defect orbitals is lifted by spin-orbit interaction into two pairs of degenerate orbitals as revealed by direct STM orbital imaging and state-of-the-art DFT and GW calculations. The exceptionally large spin-orbit splitting between the sulfur vacancy states was measured to be 252 meV, consistent with our theoretical predictions. These results suggest that the controllable introduction of chalcogen vacancies in vacuum could be used to tune the spin-valley polarization in TMDs and may be potentially used as single-photon emitters. Moreover, the reactive vacancy sites are expected to trap diffusing adatoms, hence embedding arbitrary dopants into the 2D TMD matrix. This concept could be particularly interesting to study the interaction of magnetic impurities in a highly-correlated material or
to catalytically activate the inert basal plane of TMDs.

**METHODS**

**WS$_2$/MLG/SiC CVD growth**

WS$_2$ few-layer islands were grown by a modified chemical vapor deposition process$^{32}$ on graphitized (6H)-SiC(0001) substrates. We used WO$_{2.9}$ powder (8 ppm Mo impurity concentration) and H$_2$S gas as the metal and chalcogen precursors, respectively. The growth temperature was 900 °C and the growth time was 1 h. This process lead to the formation of predominantly monolayer WS$_2$ islands on the mixed single and bilayer graphene substrate (WS$_2$/MLG/SiC). The sample synthesis is explained in detail in Ref. 33.

**Scanning probe measurements**

*STM/nc-AFM measurements.* The experiments were performed using a CreaTec low-temperature ($T \approx 5$ K), ultra-high vacuum ($p \approx 10^{-10}$ mbar) combined STM and nc-AFM. The sensor was based on a qPlus$^{34}$ quartz-crystal cantilever design operated in the frequency-modulation mode$^{35}$ (resonance frequency $f_0 \approx 30$ kHz, spring constant $k \approx 1800$ N/m, quality factor $Q \approx 60,000$, and oscillation amplitude $A \approx 1$ Å). The voltage was applied to the sample. STM images were taken in constant-current mode. STS spectra are performed in constant-height mode with a lock-in amplifier running at 670 Hz and 3 mV. The STS spectra has been characterized on Au(111) to ensure a relatively flat tip density of states. Nc-AFM measurements were acquired in constant-height mode at $V = 0$ V. The known contrast mechanism of CO-tip nc-AFM imaging enabled the unambiguous lattice site identification.$^{25,36,37}$

*Sample and tip preparation.* The CVD grown WS$_2$/MLG/SiC was annealed *in vacuo* either at about 250 °C or 600 °C for 30 min. At the lower annealing temperatures the only defects at sulfur sites were O$_5$ defects. At the higher annealing temperature, however, pristine sulfur vacancies were found as well along with O$_5$ defects (see Figs. S1,2).

The focused ion beam cut PtIr tip was sharpened by repeated indentations into a Au substrate.
A CO tip was created by picking-up a single CO molecule from the Au(111) surface\textsuperscript{38,39} located in proximity of the WS\textsubscript{2}/MLG/SiC sample.

**Density-functional theory (DFT) and GW calculations**

We first performed a density functional theory (DFT) calculation in the local density approximation (LDA)\textsuperscript{40}, with the Quantum Espresso package\textsuperscript{41}, to obtain the mean-field starting point of our GW calculation. The calculations were done with a 5×5 supercell arrangement of the WS\textsubscript{2} monolayer with one chalcogen vacancy per cell. We use a plane-wave basis and norm-conserving pseudopotentials with a 70 Ry wave function cutoff. We included the W 5s, 5p, and 5d states as valence states. The distance between repeated supercells in the out-of-plane direction was 15 Å. We fully relaxed the atomic coordinates while constraining the lattice constant to the experimental values of 3.15 Å. A 16×16×1 k-point grid was used to calculate the self-consistent charge density.

We performed GW calculations with the BerkeleyGW code\textsuperscript{42}. Our main results are obtained within the Hybertsen-Louie generalized plasmon-pole (HL-GPP) model\textsuperscript{42–44}. We used an energy cutoff of 25 Ry for the reciprocal lattice components of the dielectric matrix and included 2000 states in the summation over unoccupied states (convergence was tested with up to 20,000 states). We employed the nonuniform neck subsampling (NNS) scheme\textsuperscript{45} to sample the Brillouin zone and to speed up the convergence with respect to k-point sampling. In this scheme, we use a 3×3×1 uniform q-grid and include an additional 10 q-points in the voronoi cell around q=0, such that the smallest q-vector corresponds to 1/1150th of a reciprocal lattice. This corresponds to an effective q-grid of more than 1000×1000×1 uniform q-points and converges the QP energies within better than 0.01 eV. A truncated Coulomb interaction was used to prevent spurious interactions between periodic images of the 2D sheet\textsuperscript{46}.

To include the spin-orbit interactions we then performed a fully-relativistic noncollinear DFT calculation within Quantum Espresso, using the relaxed structure from the non-relativistic calculation. A wave function cutoff of 150 Ry was used in the fully-relativistic calculation. Then, the spin-orbit corrections at the DFT level were combined with the GW corrections following Ref. 47.
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FIGURES
FIG. 1. **Sulfur vacancy and O substituent.** a-d STM topography \((I = 20 \text{ pA}, V = 1.1 \text{ V})\) of a pristine \((V_S)\) and O-decorated \((O_S)\) sulfur vacancy in the top (a,b) and bottom (c,d) sulfur layer. e-h Corresponding CO-tip nc-AFM images of the same defects as in (a-d). The unit cell has been indicated as a guide to the eye. Yellow: S atom, blue: W atom. i-l DFT calculated defect geometry.
FIG. 2. **Sulfur vacancy defect states.**

(a) STS spectra recorded on a sulfur bottom vacancy and the pristine WS$_2$ monolayer on bilayer graphene. The valence band maximum (VBM), conduction band minimum (CBM), the Fermi level ($E_F$), the filled-states defect resonance and the unoccupied in-gap defect states are indicated.  

(b) STS spectra of the deep unoccupied V$_S$ defect states. The two zero-phonon lines (ZPL) and the subsequent vibronic side peaks are labelled. The linewidth of 9 meV (full width at half maximum) of both ZPLs gets broader for increasing phonon replica. The splitting between the ZPL peaks is due to spin-orbit coupling.  

(c) $dI/dV$ maps of the two V$_S$ defect states corresponding to the ZPL resonances of both the top and bottom V$_S$. The WS$_2$ unit cell has been indicated (to scale). Yellow: S, blue: W.
FIG. 3. **Calculated DFT and GW defect levels including SOC.** All calculations were done in a 5x5 supercell containing a single sulfur vacancy (see Methods section). **a** DFT-LDA level constant height slice of the orbital density of the in-gap defect state 8 Å above (corresponding to V$_S$ top) and 8 Å below (corresponding to V$_S$ bottom) the WS$_2$ monolayer. The WS$_2$ unit cell has been indicated (to scale). Yellow: S, blue: W. **b** Comparison of the band structure excluding and including the effect of SOC. The formerly degenerate defect state (purple) splits into two states (red and blue) with dominant contributions of $J = 3/2$ and $J = 5/2$ of the total angular momentum. **c** Comparison of the defect state energies calculated on the DFT and GW level and the corresponding experimental values (on a monolayer graphene substrate). Note that screening effects by the substrate have not been considered in the calculations. The gray boxes represent the delocalized states of the WS$_2$ layer with the conduction band minimum (CBM) and valence band maximum (VBM). The black line indicates the occupied defect resonance overlapping the valence band. The VBM of the DFT, GW calculations and the experiment has been aligned for comparability. $E_F$ indicates the experimental Fermi level.
Supplementary Information:
Large spin-orbit splitting of deep in-gap defect states of engineered sulfur vacancies in monolayer WS\textsubscript{2}

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Abstract

In this supplementary information we provide additional (i) STM and nc-AFM measurements on the distinction between the pristine and oxygen-decorated sulfur vacancy including nc-AFM simulations, (ii) STS spectra comparing the sulfur vacancy states on the mono- and bilayer graphene substrate, (iii) STS spectra and dI/dV maps of the tip-induced charging of the sulfur vacancy on monolayer graphene, (iv) STS spectra comparing the sulfur vacancy in the top and bottom sulfur layer and (v) derive the total angular momentum components of the sulfur vacancy states.

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SULFUR VACANCY VS OXYGEN SUBSTITUENT AT SULFUR SITE

In our WS$_2$/MLG/SiC sample there are five types of common point defects present after annealing at a temperature of 250 °C for 30 minutes: oxygen-substituents at S sites in the top and bottom sulfur layer (O$_S$ top and O$_S$ bottom), two tungsten site defects and a charged defect that could not be identified. At high annealing temperatures of 600 °C, sulfur vacancies in the top and bottom sulfur layer ($V_S$ top and $V_S$ bottom) form. As seen in Fig. S1, all the above mentioned defect types co-exist after the high annealing treatment and can be discriminated by their characteristic STM contrast a few 100 meV above the conduction band onset ($V = 1.1$ V in Fig. S1).

In Fig. S2 STM and nc-AFM measurements of a close $V_S$ top and O$_S$ top are shown. Images Fig. S2a,c and Fig. S2b,d depict the same defect pair. The $V_S$ top and O$_S$ top can be easily distinguished based on their STM contrast because of their distinct electronic signatures (as discussed
Figure S1. **Point defect types overview.** a-d STM topography ($I = 20$ pA, $V = 1.1$ V) of monolayer WS$_2$ after annealing to 600 °C. Along with the temperature-induced pristine vacancies, $V_S$ top and $V_S$ bottom, also the native defects $O_S$ top, $O_S$ bottom along with two defects at W sites and an unidentified charged defect were present. One defect of each type is encircled with the respective color of the legend on the right.

In CO-tip nc-AFM both defect types appear as a missing S atom in the surface sulfur layer. The O substituent is bound more closely to the W atoms (see structure model in Fig. 1j), therefore the O atom is not directly resolved as a repulsive (bright) feature in CO-tip nc-AFM. Under the same imaging conditions (identical tip and scan height) the $O_S$ appears, however, slightly more attractive (darker) as the $V_S$ top as seen in Fig. S2c,d. This (small) contrast difference is also reproduced by nc-AFM simulations based on the probe particle model$^{1,2}$ as seen in Fig. S3.

Interestingly, the presence of the $O_S$ defect has only a minimal influence on the $V_S$ defect states, not even in the nearest-neighbor configuration such as shown in Fig. S2b,d. This demonstrates the robustness of the deep in-gap states of $V_S$ against other structural imperfections that do not feature electronic states in a similar energy range.
Figure S2. **Comparison of $V_{\text{S top}}$ and $O_{\text{S top}}$ defect.** a,b STM images of two close $O_{\text{S top}}$ (left) and $V_{\text{S top}}$ (right) defects at different defect-defect separations. c,d Corresponding CO-tip nc-AFM measurements of the same defect pairs as in a and b. The O decorated S vacancy appears slightly more attractive (darker) than the pristine S vacancy in the nc-AFM image.

**TIP-INDUCED SULFUR VACANCY CHARGING ON SINGLE-LAYER GRAPHENE**

On single-layer graphene (SLG) we find a sharp feature in the STS spectra of the sulfur vacancy at negative sample bias and a significant upwards shift of the valence band (see Fig. S4a). We attribute the major resonance at negative bias around $-1.3$ V to the stationary tip-induced charging of the defect (commonly referred to as charging peak$^3$). The charging peak is identified by its energetic position shifts with tip position as illustrated in Fig. S5. The farther the tip is away from the defect (both laterally and vertically), the more the charging peak shifts towards more negative voltages. In Fig. S5a, $dI/dV(V)$ spectra are taken at different tip heights on the $V_{\text{S}}$. Only the charging peak shifts energetically. At high enough negative bias and close enough tip-sample distances, the charging peak appears in $dI/dV$ maps as a ring-like feature. In $dI/dV(z)$ spectroscopy at constant bias (Fig. S5c) the charging peak is observed at different tip heights. Charging of the defect at elevated negative biases can be explained by the voltage
Figure S3. **Nc-AFM simulation of V\textsubscript{S} and O\textsubscript{S} defects.** a-d DFT calculate defect atomic structure of V\textsubscript{S} top (a), O\textsubscript{S} top (b), V\textsubscript{S} bottom (c) and O\textsubscript{S} bottom (d). e-h Corresponding AFM simulation based on the probe particle model\textsuperscript{1,2}.

The drop across the WS\textsubscript{2} layer in the double barrier tunneling junction geometry, where at a certain threshold electrostatic field the lowest unoccupied defect state is pulled below the Fermi level of the graphene substrate. Hence, the defect gets statically negatively charged if the tip is within a certain distance from the defect, which depends on the applied bias (the more negative the bias the larger the distance). Only if the tip is within tunneling distance of the defect state, the additional electron in the defect can drain to the tip. On average the defect stays negatively charged because it is immediately refilled by electrons from the substrate. Therefore, the contrast of the dI/dV map Fig. S5b within the charging ring resembles the defect state, that is occupied by the field-induced charging, which corresponds to the lowest unoccupied defect orbital. From the lowest unoccupied defect state resonance energy (which is also field-shifted) and the charging peak energy we estimate a field induced shift of 11% of the applied bias voltage on the defect center at the chosen tunneling set point. The reported V\textsubscript{S} defect state energies in the manuscript were corrected for this shift.

No charging peak was observed for sulfur vacancies on monolayer WS\textsubscript{2} islands with a bilayer
Figure S4. **Energy shift induced by substrate.** a STS spectra recorded on a Vs bottom on monolayer WS$_2$ on single-layer graphene (SLG). A charging peak at about $-1.3$ V is observed along with an upwards shift of the valence band. b Comparison of STS on a Vs bottom defect on monolayer WS$_2$ on SLG (blue) and bilayer graphene (BLG) (red). The BLG substrate shifts the Vs resonance and conduction band minimum (CBM) towards higher energies. The biggest shift is observed at the valence band maximum (VBM), which reduces the WS$_2$ band gap on BLG. c Same defects as in b highlighting the rigid shift of the Vs defect states and the CBM between the mono- and bilayer graphene substrates.
Figure S5. **Tip-induced charging of a V$_S$.** a STS spectra recorded on a V$_S$ top at different tip heights. The charging peak around $-1.3$ V shifts towards more negative values for increasing tip-defect separations. a dI/dV map at $-1.45$ V. The charging peak is visible as a circular feature around the defect. Inside the ring, the defect is charged at this bias, outside it is neutral. c dI/dV intensity at $-1.3$ V recorded as a function of tip height across the defect. d STS spectra recorded across the V$_S$. The V$_S$ position in c and d is indicated by the vertical dashed line.

graphene (BLG) substrate. As seen in Fig. 2 of the manuscript and Fig. S4b, the STS spectra of V$_S$ on BLG features an increase of the DOS around the VBM, but no signatures of defect charging. The qualitatively different behavior between mono- and bilayer graphene substrates can be explained by the energetic shift of the band structure induced by screening effects and a change in work function$^{4,5}$. This combined effect shrinks the WS$_2$ band gap and shifts the VBM and CBM towards higher energies for WS$_2$ on BLG. As seen in Fig. S4c, the V$_S$ defects states
and the CBM are rigidly shifted by about 160 mV towards higher energies for BLG. Hence, the tip-induced band bending at negative bias as described in the previous paragraph is, in the case of the BLG substrate not high enough to pull down the lowest $V_S$ defect state below the Fermi level. Therefore, no tip-induced charging is observed.

**SULFUR TOP VACANCY VS SULFUR BOTTOM VACANCY**

The electronic signature of the top and bottom sulfur vacancy are essentially equivalent as evident from the STS spectra shown in Fig. S6. This indicates no significant hybridization of the $V_S$ defect states with the underlying graphene substrate exists. A small shift of the defect state energies on the order of 20 meV is observed, which we attribute to the substrate electronic inhomogeneity. This position dependent shift acts on the entire spectrum, hence the relative energetic position of the defect state with respect to the conduction band onset stays constant.

**TOTAL ANGULAR MOMENTUM COMPONENTS OF $V_S$ LOCALIZED IN-GAP STATES**

Fig. S7 shows the DFT projected density of states (PDOS) of states on atomic orbitals with a significant contribution to the defect states. Each subplot shows contributions from an atomic orbital with a specific orbital angular momentum, $L$, and total angular momentum, $J$, with the colored area proportional to the contributions from states with different secondary total angular momentum numbers, $m_j$. Each doubly-degenerate state has equal contributions from $+m_j$ and $-m_j$, as the degeneracy arises as a consequence of Kramers theorem in the presence of time-reversal symmetry. Hence, unlike the bulk VBM, the defect states exhibit no spin polarization. To emphasize this point, Table I shows the contribution to the total density of states from a subset of the angular momentum eigenstates with the largest contribution.

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Figure S6. **Comparison of dI/dV spectra of VS top and VS bottom.**  

- **a** dI/dV spectrum of VS top and the bare WS$_2$ on a SLG substrate.  
- **b** dI/dV spectrum of VS bottom and the bare WS$_2$ on a SLG substrate.  
- **c** Direct comparison of the in-gap defect states of VS top and bottom on the same island. The small rigid shift of the spectrum (including the onset of the valence and conduction band) can be explained by the substrate electronic inhomogeneity, which is on the order of 20 meV. Since the splitting and broadening of the top and bottom VS is essentially the same, significant substrate hybridization effects can be excluded.
Figure S7. The projected density of states on atomic orbitals with a significant contribution to the defect states: a) W "5d" orbitals with J=2.5, b) W "5d" orbitals with J=1.5, c) W "6p" orbitals with J=1.5, d) W "6p" orbitals with J=0.5, e) S "3p" orbitals with J=1.5, and f) S "3p" orbitals with J=0.5. The colored area in each plot is proportional to the contribution from states with the secondary total angular momentum quantum number $m_j$ for a given total angular momentum J.

Table I. Orbital contributions of the total angular momentum eigenstates $|J, m_j\rangle$ of S and W atoms to the lower ($E_1$) and higher energy ($E_2$) S vacancy state. Considering a general form of the sulfur vacancy states: $|\Psi\rangle = \sum_{J,m_j} c_{J,m_j} |J, m_j\rangle$, the table specifies the number $\sum_{J} c_{J,m_j}$ for each $m_j$ component. The expectation value $\langle J_z \rangle = \sum_{J,m_j} c_{J,m_j} |c_{J,m_j}|^2 \cdot h m_j$ is vanishing for both defect states.

| $m_j$   | +5/2 | +3/2 | +1/2 | -1/2 | -3/2 | -5/2 | $\langle J_z \rangle$ |
|---------|------|------|------|------|------|------|----------------------|
| $E_1$   | 0.04 | 0.51 | 0.42 | 0.42 | 0.51 | 0.04 | 0.00                 |
| $E_2$   | 0.32 | 0.22 | 0.43 | 0.43 | 0.22 | 0.32 | 0.00                 |
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