Optical identification of sulfur vacancies: Bound excitons at the edges of monolayer tungsten disulfide

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Defects play a significant role in tailoring the optical properties of two-dimensional materials. Optical signatures of defect-bound excitons are important tools to probe defective regions and thus interrogate the optical quality of as-grown semiconducting monolayer materials. We have performed a systematic study of defect-bound excitons using photoluminescence (PL) spectroscopy combined with atomically resolved scanning electron microscopy and first-principles calculations. Spatially resolved PL spectroscopy at low temperatures revealed bound excitons that were present only on the edges of monolayer tungsten disulfide and not in the interior. Optical pumping of the bound excitons was sublinear, confirming their bound nature. Atomic-resolution images reveal that the areal density of monosulfur vacancies is much larger near the edges (0.92 ± 0.45 nm−2) than in the interior (0.33 ± 0.11 nm−2). Temperature-dependent PL measurements found a thermal activation energy of ~36 meV; surprisingly, this is much smaller than the bound-exciton binding energy of ~300 meV. We show that this apparent inconsistency is related to a thermal dissociation of the bound exciton that liberates the neutral excitons from negatively charged point defects. First-principles calculations confirm that sulfur monovacancies introduce midgap states that host optical transitions with finite matrix elements, with emission energies ranging from 200 to 400 meV below the neutral-exciton emission line. These results demonstrate that bound-exciton emission induced by monosulfur vacancies is concentrated near the edges of as-grown monolayer tungsten disulfide.

INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs) have been studied intensively for their extraordinary electronic and optical properties (1, 2), such as acquiring a direct bandgap when thinned down from the bulk (3), hosting strong electron-hole Coulomb interactions (4, 5), and supporting a variety of many-body states beyond excitons (6, 7). Their intriguing optical properties have opened prospects for a broad range of applications, including valleytronics (8, 9), photosensors (10), and nanocavity lasers (11).

The near-bandgap optical properties of TMDs are governed by excitons. Although neutral excitons are typically mobile, both neutral and charged lattice defects can bind electron-hole pairs to form so-called bound excitons. The finite binding energy between the neutral exciton and the defect creates a bound-exciton peak XB in the PL spectrum at an energy value smaller than the neutral-exciton peak X0 (4, 12–14). Previous works reported a bound-exciton feature in the photoluminescence (PL) spectrum of defective exfoliated TMDs after exposure to α irradiation or oxygen plasma treatment (12, 15), as well as in pristine exfoliated samples (8, 12, 16, 17). Defects in the TMD family have also been characterized on samples synthesized by chemical vapor deposition (CVD) (18–24). However, a quantitative study of the bound exciton’s thermal stability, dynamics, and dependence on defect density remains absent and is explored here.

We investigate bound-exciton emission in CVD-grown triangular islands of monolayer tungsten disulfide (WS2), with particular focus on the differences between the interior regions and edges of the island. We report a direct spatially resolved observation of two bound-exciton transitions XBi and XB2 at the edge of the triangular islands. Atomically resolved images showed a high monosulfur vacancy concentration of 0.92 ± 0.45 nm−2 near the edges, in contrast to 0.33 ± 0.11 nm−2 in the interior. First-principles calculations confirmed that sulfur vacancies introduce midgap states that are tightly localized near sulfur vacancies, suggesting that excitons can bind more strongly to these localized charged defects than to free charge carriers. The calculated finite matrix elements between the defect states and valence band states imply that the radiative recombinations of the exciton through this channel is allowed and observable in the PL spectra. Under optical pumping, the intensity of the bound-exciton peaks shows a sublinear dependence on the laser intensity, verifying their bound nature. Whereas the bound-exciton peak XB2 is ~300 meV below the neutral-exciton peak, temperature-dependent PL experiments determined the thermal activation energy of XB2 to be only ~36 meV. To resolve this apparent paradox, we propose that the decay process involves the thermal dissociation of the bound exciton into a neutral exciton and the charged defect.

RESULTS

Monolayer WS2 samples were grown by CVD on 300-nm SiO2/Si substrates, as detailed in Materials and Methods. The samples were then characterized by atomic force microscopy (AFM), Raman spectroscopy, scanning electron microscopy, and PL at room temperature (see fig. S1). The 1H-WS2 structure is a sandwich of W atoms between two hexagonal layers of S atoms (S-W-S) with a trigonal prismatic coordination ($D_{3h}$, point group) (25). An atomically resolved image acquired from an
area in the interior of a triangular island, where the defect density is lower than that near the edge, shows this 1H-WS₂ structure (Fig. 1A).

Figure 1B shows an optical image of the grown WS₂ that is selected for further investigation; note that the triangular monolayer region is green, and the thicker regions are yellow. Figure 1C shows three PL spectra, which are normalized by the intensity of the neutral exciton, taken from the marked regions in Fig. 1B: The circle and square are from the edges, and the triangle is from the interior. The spectra were acquired at 77 K using a 488-nm laser excitation. We used a power density of 9 kW cm⁻², which is low enough to avoid the creation of trions by heating (26). The X₀ peak in the interior (triangle) is sharp, with a full width at half maximum (FWHM) of Γ₀ ≈ 23 meV; this indicates an absence of trions either due to a negligible degree of n-doping or a high degree of compensation (that is, n-carriers can be depleted by the S vacancy sites near the center), where the density of sulfur vacancies is lower than the edge regions (see Fig. 2A) but possibly enough to deplete the n-carriers.

For the other locations, the neutral-exciton peaks red shift by 10 meV (square) and 20 meV (circle), as compared to the interior. This shift has been ascribed to bandgap renormalization modulated by defect density (27).

In contrast to the interior, the PL spectra around 2050 meV at the two edges (circle and square) have asymmetric line shapes that suggest the presence of bound excitons (see fig. S2 for the decomposition of the peaks). The shoulder, which is identified here as bound exciton X₂, only emerged when the bound-exciton peak X₂ centered at ~1750 meV also appeared. The bound-exciton binding energy is defined as the energy difference between the neutral exciton and the bound exciton as follows: ΔX₂ = Eₓ₀ − Eₓ₀. The binding energies were ΔX₀ = ~29 and ~35 meV at the square and circle, respectively, whereas ΔX₂ = ~300 meV for both edge locations. Although the measured ΔX₀ are close to the reported trion binding energy (4, 28), we will confirm in the next section that the emission is indeed from a bound exciton.

We performed spatially resolved PL measurements at low temperatures to further investigate the bound exciton in monolayer WS₂. The incident light spanned from 2140 to 2340 meV, whereas reflected light was collected using two band-pass filters centered at 1970 and 1690 meV. Figure 1 (D and E) shows the PL intensity map at 77 K for the X₀ peak (centered at 1970 meV) and the X₂ peak (centered at 1690 meV). The intensity of the neutral exciton is relatively homogeneous, whereas the bound-exciton intensity is highly localized at the edges of the WS₂ island. This behavior is also visible in the intensity profiles of Fig. 1F acquired along the dashed lines in Fig. 1 (D and E). Additional PL images taken at 77 K can be found in fig. S3. This is the first direct evidence of bound excitons in as-grown monolayer TMDs.

To investigate the structural differences between the interior and edge regions of WS₂ triangles at the atomic scale, we performed scanning transmission electron microscopy (STEM). Before STEM imaging, a WS₂ triangle was transferred to a QUANTIFOIL gold grid with a holey carbon film (Fig. 2A, left). The interior and edge regions marked by circles in Fig. 2A were investigated by STEM—annular dark field (ADF) imaging. Mainly, two types of defects were observed in both regions: monosulfur vacancies (Vₛ₅ yellow circle in Fig. 2A) and occasional WS₃ vacancies (V_WS₃ orange triangle in Fig. 2A). More Vₛ were found in the edge regions, and they tend to aggregate. Other types of defects, such as W vacancies (V₇), disulfur vacancies (V_WS₂), and antisite defects, such as S₂ substituting a W site (S₂W) or its opposite (WS₂S), were only very rarely observed. To obtain STEM-ADF images with higher contrast from sulfur atoms, we used a low-angle ADF (LAADF) condition. Under this condition, the ADF intensity includes both Z contrast and diffraction contrast; defect structures were confirmed by comparing ADF images with simulated STEM images, as shown in Fig. 2B. Vₛ and V_WS₃ have been previously reported for monolayer MoS₂ (25). Here, we focus on the density of Vₛ because the density of V_WS₃ defects is much lower.

To estimate and compare Vₛ density between two regions, we compared a line profile of ADF intensity with its simulation. Several images were recorded from different locations in both regions to obtain statistical data. For the edge region, images were acquired from more than one triangle at randomly selected locations within a distance of 1.0 µm

Fig. 1. Bound excitons at the edges. (A) Atomic structure of monolayer 1H-WS₂. Scale bar, 1 nm. (B) Optical image of triangular WS₂ islands. (C) PL spectra obtained from the marked regions in (B). PL intensity image at 77 K of (D) X₀ peak centered at ~1970 meV and (E) X₂ peak centered at ~1690 meV. Scale bars, 10 µm. (F) X₀ and X₂ intensity profiles acquired along the dashed lines in (D) and (E), respectively. arb. units, arbitrary units.
as a function of the neutral-exciton intensity. We obtain defect densities of 0.33 ± 0.11 and 0.92 ± 0.45 nm⁻² from the actual edge. We obtain defect densities of 0.33 ± 0.11 and 0.92 ± 0.45 nm⁻² in the interior and near the edge, respectively (Fig. 2C). The higher Vₛ defect density in the edge region is consistent with our observation of bound excitons at the edge and also with previous reports on defect distribution in monolayer MoS₂ (27). These Vₛ defect densities are much higher than reported values for CVD-grown MoS₂ (~0.12 nm⁻²) (29).

To verify that $X^{B,2}$ indeed involves excitons bound to the defects, we investigated exciton population as a function of the incident laser power density ranging from 9 to 230 kW cm⁻² at 77 K, using continuum wave excitation at 488 nm. Figure 3 (A and B) depicts the low-energy spectral range of 77 K acquired from the interior and edge regions on a different sample from Fig. 1B. The neutral-exciton energy (~2050 meV) did not change as a function of laser power density. However, the Lorentzian width $\Gamma_{EX}$ of $\Delta$ increased with increasing laser intensity, broadening by ~3 and ~6 meV for the interior and edge areas, respectively. The increased broadening observed from the edges could be related to bound-exciton emission $X^{B,1}$.

The insets in Fig. 3 (A and B) display the low-energy spectral range marked by the dashed rectangle around 1750 meV. The absence of a bound exciton in the interior of the triangle confirms that the higher laser intensities did not create these defects in the high-quality regions. In contrast, the bound exciton is clearly observed near the edges of the triangle. Figure 3C shows a logarithmic plot for the intensity of the bound-exciton transitions $I_{XB}$ and $I_{XB}$, which is obtained from the edge region (Fig. 3B) as a function of the neutral-exciton intensity $I_{EX}$. The data can be fitted by a power law of the form $I_{XB} \propto (I_{EX})^\alpha$ with $\alpha = 1.09 \pm 0.01$ and $I_{XB} \propto (I_{EX})^\alpha$ with $\alpha = 0.16 \pm 0.01$, as shown in Fig. 3C. The sublinear trend for $X^{B,2} (\alpha = 0.16)$ is a signature of emission from bound excitons, because defect sites in the lattice become saturated with trapped excitons at higher laser intensities (12, 16, 30).

For the nature of the $X^{B,2}$ feature, its energy, being lower than that of the free exciton, indicates that it originates from excitons bound to other structures or quasi-particles (by a binding energy of $E_{EX} - E_{XB}$). If excitons bind to free charge carriers (forming free trions), the expected exponent from theory is 1.5 (31). However, the measured value for this exponent that is reported in the literature (30–32) for WS₂ ranges from 0.9 to 1.4, consistent with our measured value of 1.09. It was suggested by He et al. (32) that the smaller value (<1.5) indicates excitons bound to lattice defects, whose identity we propose in the following.

As mentioned above, bound excitons emerge when defects such as sulfur vacancies trap neutral excitons at low temperatures. The thermal stability of this complex depends on the activation energy that binds the neutral exciton to the defect (33–36). Figure 4A shows the variation in PL intensity ranging from 77 to 113 K acquired at the edge using a power density of 9 kW cm⁻², which is normalized by the neutral-exciton peak at 2050 meV. The white dashed line traces the position of $X^{B,2}$, and the PL spectra for five temperatures are replotted in Fig. 4B. The $X^{B,2}$ peak at ~1750 meV decreases in intensity as the temperature increases and disappears above 107 K.

To estimate the thermal activation energy, we consider a simple rate equation for bound-exciton dynamics as follows: $dN/dt = \beta - \gamma N$, where $N$ is the density of bound excitons, $\beta$ is their formation rate (assumed to
be temperature-independent), and the decay rate $\gamma$ is temperature-dependent according to

$$
\gamma = \tau^{-1} + C e^{-E_A/(k_B T)}
$$

where $\tau$ is the lifetime of the bound exciton, $C$ is a prefactor, and $E_A$ is the thermal activation energy $^{(37)}$. The PL intensity $I_{X^B}$ of the bound exciton in steady state is proportional to $\gamma^{-1}$. Figure 4C shows the normalized PL intensity $I_{X^B}$ as a function of temperature along with a fit to Eq. 1, where we find $\tau = 56$ ns, $C = 5.5 \times 10^5$ s$^{-1}$, and $E_A = 36 \pm 6$ meV.

The deviation of the measured PL intensity from the fit above 100 K may be attributed to the low signal-to-noise ratio of the bound-exciton peak at that temperature range or to other unidentified excitonic levels at higher energies than the neutral-exciton level that can host additional thermally activated decay pathways. Surprisingly, the thermal activation energy of $X^B$ is much smaller than its binding energy $\Delta_{X^B} = 300$ meV but close to the binding energy of $X^0$, $\Delta_{X^0} \approx 32$ meV. We propose that at low temperatures, neutral excitons bind to negatively charged sulfur vacancies by 36 meV, forming a defect-bound exciton that consists of one valence band hole, one conduction band electron, and one electron at the defect state ($\sim 300$ meV below the conduction band minimum). Two types of emissions are expected from the defect-bound exciton: Recombination of the electron localized at the defect with the valence band hole contributes to the $X^B$ peak, whereas the recombination of the conduction band electron with the valence band hole contributes to the $X^0$ peak. As the temperature increases, this defect-bound exciton dissociates into a neutral exciton and an electron remaining at the defect site $^{(38)}$, leaving only the $X^0$ peak corresponding to the neutral-exciton recombination. In addition, the temperature dependence of the PL peak position for the neutral exciton $X^0$ was studied from the spectra acquired from the interior and at the edges, as shown in fig. S4; the similar behavior of the $X^0$ peaks in the interior and at the edge supports the conclusion that it is unrelated to the defects (see the Supplementary Materials for details).

We performed density functional theory (DFT) calculations (see Materials and Methods) to investigate the electronic structure and optical response of WS$_2$ monolayers containing sulfur vacancies. The band structure of a $5 \times 5$ WS$_2$ supercell containing one sulfur vacancy is shown in Fig. 5A, along with the projection of the wave function onto the atomic orbitals of the nearest-neighbor tungsten sites of the sulfur vacancy, which is represented by the red component of the colored bands. The vertical arrows indicate the optical transitions for the neutral exciton $X^0$ and the bound exciton $X^B$ (or more precisely, the band transitions most closely associated with these processes). The midgap state is tightly localized near the sulfur vacancy. The root mean square radius of the partial charge density of the defect state is 0.95 lattice constant, which is smaller than the typical (~3 lattice constants) radius of neutral
excitons in monolayer TMDs (6). Thus, if this state is charged (which is consistent with most of the CVD-grown WS2 samples being n-doped), the binding of a neutral exciton to this localized charged defect can be more stable than the binding to free charge carriers (forming free trions).

The quantitative estimate of the emission energy from the defect bands to the valence bands cannot be properly described by directly taking Kohn-Sham eigenvalues of the defect states, but instead, it requires a correct evaluation of the energetics of charged defects because any optical transition to or from the defect state involves a change in its charge transition energy referenced to the conduction band (CB) minimum; the thermodynamic transition energy for the charged states \( q = 0 \) as a function of the Fermi energy within the bandgap and is thus omitted for clarity). The \( \epsilon(0/−1) \) transition energy lies 0.33 eV below the conduction band minimum.

\( \epsilon(0/−1) \) reflects the energy difference between two charged states in their respective equilibrium configurations: the \( q = −1 \) state relaxed into configuration \( \{R\}_q = −1 \) and the \( q = 0 \) state relaxed into \( \{R\}_q = 0 \), as shown schematically in Fig. 5E, where the horizontal axis \( \{R\} \) represents the collective ionic coordinates of the system. Optical transitions occur on much shorter time scales than lattice relaxation; therefore, optical transition energies were evaluated with fixed atomic positions, as described below. After an electron is excited to the conduction band and decays into a defect state \( D' \), it can decay radiatively to the valence band \( e_{VB} \), leaving behind a neutral defect \( D' \) (jointly denoted as \( D' + e_{VB} \) in Fig. 5E).

Among the possible emission dynamics, two extreme cases are considered (39): (i) If this decay occurs very quickly after occupation of the \( D' \) state, then the \( D' \) state retains the \( \{R\}_q = 0 \) atomic configuration of its progenitor \( D' \) state, that is, it emits a photon at \( E_{F1,1} \) (blue arrow); this energy can be determined from the \( (0/−1) \) charge crossover when both states are held at the equilibrium configuration for \( q = 0 \) (dashed blue line in Fig. 5D). (ii) If the electron occupies \( D' \) long enough to relax into its equilibrium position \( \{R\}_q = −1 \), then the subsequent emission will occur at sulfur vacancies in WS2 only support stable formation of \( q = 0 \) and \( −1 \) vacancies as the Fermi energy is varied from the valence band edge, similar to a previous study on MoS2 (43) (the \( q = −2 \) state is found to be less favorable for all Fermi energies within the bandgap and is thus omitted for clarity). The \( \epsilon(0/−1) \) transition energy lies 0.33 eV below the conduction band minimum.

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with initial and final states held at the $[R]_{ij} = -1$ configuration [orange arrow and dashed line in Fig. 5 (D and E)]. These extreme cases bracket a range of allowed emission energies between $E_{\text{PL1}}$ and $E_{\text{PL2}}$, which are 0.42 and 0.21 eV below the conduction band edge. Finally, assuming that the neutral-exciton binding energy is comparable to the total defect-bound exciton binding energy (that is, the binding between a neutral exciton and a charged defect is much weaker than the neutral-exciton binding energy), we can infer that the emission energy of the bound exciton is also approximately 420 to 210 meV below the neutral-exciton emission energy. This is consistent with the peak position and broad linewidth of the bound-exciton peak, which spans from 200 to 400 meV below the neutral-exciton emission energy. Because the above broadening mechanism requires an excitation lifetime comparable to the lattice relaxation time (which must exceed the characteristic phonon period), lifetime broadening is negligible in this scenario, as compared to the observed width. Lifetime broadening of a shorter-lived excited state and/or inhomogeneous broadening could also be considered in alternative scenarios.

To determine whether the transition from the defect state $X_{B1}$ is optically active, we also calculated the optical transition matrix elements between the valence band state and the conduction or defect band state of a $5 \times 5$ WS$_2$ supercell containing one sulfur vacancy, as shown in Fig. 5B. That is, we assume that the optical transition matrix element between two many-body states (before and after electron-hole recombination) mainly consists of matrix elements between single-particle valence band states and defect/conduction band states [by expanding many-body states into single-particle electron-hole pairs, under the Tamm-Dancoff approximation (44)]. The magnitude of the matrix element for each vertical transition is represented by the radius of a pair of circles marking the initial and final states for that transition, the color of those same circles representing the energy of that transition. Apart from the expected large matrix element between the valence band maximum and conduction band minimum at the K point, the matrix elements between the highest valence band and the defect bands are also significant, indicating possible channels of bound-exciton recombination. We further calculated the imaginary part of the dielectric function $\epsilon_{\text{im}} = \epsilon_{\text{pp}}$ in a $5 \times 5$ WS$_2$ supercell with and without one sulfur vacancy, as shown in Fig. 5C. Because of the relatively large size of these systems, the dielectric function was calculated within the random phase approximation (RPA) without including local field effects (45). The bandgap calculated at the DFT-RPA level, which is 1.82 eV, is underestimated but happens to agree better with the PL measurement than the quasi-particle bandgap because of a partial and fortuitous cancellation of quasi-particle effects and the exciton binding energy (46, 47); compared to the calculated quasi-particle bandgap of 3.22 eV, the original DFT gap of 1.82 eV is actually closer to the calculated gap of 2.13 eV that is obtained when both quasi-particle effects and the electron-hole interaction are taken into account (see Materials and Methods).

The JDOS in the $5 \times 5$ structure is also superimposed as filled plots: Red (gray) curves are the JDOS from the three highest valence bands to the two defect (six lowest conduction) bands. As expected, the defect states introduce an additional low-energy feature at ~1.5 eV, corresponding to the transition $X_{B1}$. To rule out the possibility that the bound-exciton states are introduced by adsorbed gas molecules during the PL experiment (conducted in ambient nitrogen), the interactions between sulfur vacancies and two types of gas molecules, nitrogen and oxygen (from residual oxygen), are also modeled within DFT (see fig. S5). An N$_2$ molecule is found to physically adsorb onto the vacancy site and introduces no new levels near the band edges or midgap in the WS$_2$ system, whereas an O$_2$ molecule is found to strongly bind to a vacancy site, significantly altering the orbital characters of the band edge states, but it only introduces midgap states within ~100 meV of the conduction band minimum. Hence, neither gas molecule is expected to induce the observed defect-bound excitons ~300 meV below the neutral-exciton energy. The electronic structure and the optical response of another type of point defect frequently observed in STEM images, WS$_3$ vacancies, are also discussed in fig. S6. Although WS$_3$ vacancies introduce midgap states 0.3 to 0.9 eV below the conduction band minimum and have finite optical transition matrix elements with the valence band edge states, they are not expected to dominate the optical spectra because they are estimated to be 25 times less common than sulfur vacancies on the basis of STEM image analysis.

The $X_{B1}$ and $X_{B2}$ features may also be assigned to donor-bound excitons and acceptor-bound excitons in an $n$-$p$ compensated sample because their levels appear to align with donor and acceptor levels introduced by Re substitutions and S vacancies recently identified in bulk MoS$_2$ samples (48). However, the proposed assignment appears inconsistent with the thermal activation energy anomaly mentioned above. If the number of donors is not larger than the number of acceptor levels, $N_d \leq N_a$ then all the donor (acceptor) levels would be depleted (filled); thus, a thermal energy of ~30 meV would not be enough to ionize the electrons bound at the deep acceptor levels. If $N_d > N_a$, then a thermal energy of ~30 meV would ionize the donor electrons, possibly giving rise to $X_{B1}$, but it is not apparent how the suggested assignment would lead to the estimated thermal activation energy of ~30 meV for $X_{B1}$, which lies ~300 meV below the band edge, as we have observed for our samples.

**DISCUSSION**

In summary, the interior and edge regions of as-grown monolayer WS$_2$ triangular islands have been investigated using PL spectroscopy, scanning electron microscopy, and first-principles calculations. In the PL spectra at low temperature, two additional features $X_{B1}$ and $X_{B2}$ corresponding to bound excitons can be observed only at the edges and not in the interior. A lower density of monosulfur vacancies in the interior ($0.33 \pm 0.11 \text{ nm}^{-2}$) was confirmed by atomic-resolution images, as compared to a much larger concentration near the island edges. Optical pumping experiments revealed a sublinear behavior for both bound-exciton transitions when increasing the power density, which is a signature of defect-bound species. In addition, temperature-dependent PL measurements showed that a bound exciton dissociates into a neutral exciton and a negative defect at relatively low temperatures (ca. 107 K). First-principles calculations of defective WS$_2$ reveal a finite optical transition matrix element between the highest valence band and the midgap states introduced by sulfur vacancies.

**MATERIALS AND METHODS**

**Chemical vapor deposition**

Triangular monolayers of WS$_2$ were grown at atmospheric pressure at 700°C on Si wafers with a 300-nm SiO$_2$ layer. An alumina boat containing 400 mg of sulfur (Alfa Aesar, 99.5%) was located upstream and independently heated using a heating belt. Ten milligrams of WO$_3$ powder (Alfa Aesar, 99.998%) was placed directly on a SiO$_2$ substrate, and another wafer was placed directly on top of the SiO$_2$ and then placed inside of a quartz tube with a diameter of 2 cm. The furnace was
heated to 500°C over 15 min, heated again to 700°C over 15 min, and held at that temperature for 15 min and, subsequently, was allowed to cool to room temperature. The sulfur powder was heated separately. First, it was heated to 700°C over 10 min with a subsequent 15-min dwell time and then ramped up to 250°C over 5 min with a 15-min dwell time, followed by naturally cooling down to room temperature. The quartz reaction tube was flushed with 300–standard cubic centimeter per minute (SCCM) high-purity argon for 10 min to remove oxygen before starting the growth process. The argon flow rate was set to 200 SCCM during the growth. Monolayer WS$_2$ triangles grew on both the bottom and top substrates.

### Raman and PL spectroscopy

The Raman and PL spectra were acquired using a Renishaw inVia microscope with Coherent Innova 70C argon-krypton laser at 488 nm, and backscattering configuration was performed using a 1800-line/mm grating. Laser power density was measured with a Thorlabs optical power meter. We used the following equation to calculate the incident light intensity: $I = (4\pi P r^2) (1 - \frac{d}{\lambda})$, where $P$ is the measured power of the incident laser beam, and $d$ is a numerical aperture of the objective used. An Olympus 50x objective lens with a 0.50 NA was used. PL microscopy images were obtained using Zeiss Axio Scope.A1. The incident light was selected in the region of 2140 to 2304 meV, and the reflective light was selected using a band-pass filter centered at 1960 meV (FWHM = 124 meV) for neutral excitons and a band-pass filter centered at 1653 meV (FWHM = 88 meV) for bound excitons. An Olympus 50x objective lens with a 0.45 NA was used. We used a Linkam THMS600 optical stage to scan a temperature range of 300 to 77 K; these measurements were acquired in ambient nitrogen.

### Scanning electron microscopy

High-quality field-emission scanning electron microscopy images of monolayer WS$_2$ triangles on SiO$_2$ were acquired in a dual-beam microscope (FEI Helios NanoLab 660). Enhanced contrast was achieved by using a low acceleration voltage (2 kV) and collecting the secondary electrons with a through-lens detector instead of an Everhart-Thornley detector.

### Scanning transmission electron microscopy

WS$_2$ triangles grown on the SiO$_2$ substrate were transferred to a QUANTIFOIL gold TEM grid. Poly(methyl methacrylate) (PMMA) was spin-coated onto WS$_2$ triangles as a supporting film during transfer. The SiO$_2$ layer was etched away by soaking the substrate in 1 M sodium hydroxide (NaOH) aqueous solution; the PMMA/WS$_2$ triangle film was cleaned using distilled water several times, followed by fishing out of the film with the QUANTIFOIL grid. After the film was completely dried, the PMMA layer was cleaned using acetone and isopropanol. STEM was carried out by FEI Titan3 G2 S/TEM operating at 80 keV. To reduce irradiation damage, we kept the beam current below 40 pA. A high-angle ADF (HAADF) detector was used for STEM-ADF imaging. To enhance the contrast from sulfur atoms to ensure accurate counting of monosulfur vacancies, we used a LAADF condition rather than an HAADF condition. For most images in the text, a Gaussian blur filter was applied by the ImageJ program to reduce noise and enhance the visibility of structural details, but raw images were used to acquire line profiles of ADF intensity. STEM-ADF image simulation was conducted by the QSTEM package (49). Simulation parameters, such as acceleration voltage, spherical aberration ($C_3$ and $C_4$), and convergence angle and inner/outer angle for the HAADF detector, were set according to the experimental conditions.

### Atomic force microscopy

The AFM measurements were performed in a semicontact tapping mode, using silicon nitride tips with a MFP-3D AFM (Asylum Research).

### First-principles calculations

DFT calculations were performed with the generalized gradient approximation by Perdew, Burke, and Ernzerhof (GGA-PBE) (50) using the projector augmented wave method (51, 52), as implemented by Vienna Ab initio Simulation Package (53, 54). All calculations were converged at a plane wave expansion energy cutoff of 400 eV and an atomic force convergence threshold of 0.02 eV/Å. Long-range dispersion forces were included using the semiempirical DFT-D2 method (55).

The optical gap of pristine WS$_2$ was calculated by solving the Bethe-Salpeter equation (BSE) (44) based on the quasi-particle band structure obtained at the $G_0W_0$ level (56), as implemented by the BerkeleyGW package (57). Spin-unpolarized Kohn-Sham orbitals and eigenvalues were obtained with the GGA-PBE functional (50) using the Quantum ESPRESSO package (58). A cutoff energy of 12 Ha and 300 bands were used to evaluate the dielectric matrix and the self-energy. The BSE direct and exchange kernels were calculated on a $12 \times 12 \times 1$ grid and interpolated onto a finer $36 \times 36 \times 1$ grid for diagonalization.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/4/e1602813/DC1

Characterization of the WS$_2$ triangles

PL spectroscopy at low temperature

Density functional calculations of gas adsorption and WS$_2$ vacancy

fig. S1. Details on the characterization of the WS$_2$ monolayer.

fig. S2. The decomposition of the PL spectra.

fig. S3. PL images at low temperature.

fig. S4. Temperature-dependent PL for the interior and edge regions.

fig. S5. Band structure of a 5 × 5 WS$_2$ supercell with an N$_2$ or O$_2$ molecule adsorbed on the surface at a sulfur vacancy site.

fig. S6. Band structure of a WS$_2$ vacancy within a 5 × 5 supercell.

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Minas Gerais (FAPEMIG). **Author contributions:** V.C. performed the PL measurements. K.F. and B.K. performed the STEM measurements. Y.W. performed the first-principles calculations. A.M. performed the Raman measurements. S.F. performed the AFM measurements. Z.L. and C.Z. synthesized and characterized the materials. N.P.-L. performed the scanning electron microscopy measurements. V.C., Y.W., and K.F. analyzed the data. V.C., Y.W., K.F., B.R.C., A.L.E., V.H.C., and M.T. wrote the manuscript. All authors commented on the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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