The origin of single photon emission in 2D WSe₂

Yu Jie Zheng¹,², †, Yifeng Chen², †, Yu Li Huang¹,³, Pranjal Kumar Gogoi¹, Ming Yang Li⁴, Lain-Jong Li⁴, Paolo E. Trevisanutto², Qixing Wang¹, Stephen J Pennycook⁵, *, Andrew Thye Shen Wee¹,², *, Su Ying Quek¹,², *

¹Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore

²Centre for Advanced 2D Materials, National University of Singapore, Block S14, Level 6, 6 Science Drive 2, 117546, Singapore

³Institute of Materials Research & Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, 138634, Singapore

⁴Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

⁵Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575

†: These authors contributed equally to this work.

Corresponding Authors *: phyqsy@nus.edu.sg (theory); phyweets@nus.edu.sg (STM); msepsj@nus.edu.sg (STEM)
Abstract

Several experimental groups have shown that defect structures in 2D WSe₂ result in single photon emission (SPE). However, the origin of SPE is still unknown. We present a first principles study of the nature and optical properties of point defects in 2D WSe₂, together with scanning tunneling microscopy (STM) and scanning transmission electron microscopy images. We predict that O₂ can dissociate easily at Se vacancies, resulting in O-passivated Se vacancies (OSe) and O interstitials (Oins), which give STM images in good agreement with experiment. Our GW-Bethe-Salpeter-equation calculations show that Oins defects give exciton peaks ~50-100 meV below the free exciton peak, in good agreement with the localized excitons observed in independent SPE experiments. No other point defect (OSe, Se vacancies, W vacancies, and Se₇W antisite defects) gives excitons in the same energy range. We conclude that the Oins defect is a source for the SPE previously observed in 2D WSe₂.
Solid-state single photon light sources are fundamental to the development of next
generation photonic devices\(^1\). 2D semiconductors have emerged as solid-state host
systems for quantum emitters and exhibit potential for scalable quantum information
processing. Hexagonal boron nitride and the transition metal dichalcogenide (TMD),
WSe\(_2\), are to date the most promising 2D material quantum emitters\(^1\). Prior to the
interest in 2D semiconductors, nitrogen-vacancy centres in diamond have been found
to be quantum emitters, and their electronic properties have been studied extensively\(^1\).
Knowledge of the source of SPE is a necessary first step to understand and control the
emission of single photons. However, for 2D materials, the origin of SPE is still
unknown. Studies of quantum emitters in other systems have concluded that exciton
localization is required for quantum emission\(^2\), and therefore, point defects are a
candidate source of SPE in 2D materials.

In this work, we identify point defects in single layer (SL)-WSe\(_2\), and predict their
optical properties. Several independent groups have measured SPE from SL-WSe\(_2\),
with the energy of localized excitons ~45-100 meV below the free exciton A peak in
SL-WSe\(_2\)\(^3, 4, 5, 6, 7, 8\). SPE arises from edge sites in some experiments\(^5, 7\), and from the
interior of the flakes in others\(^3, 4\). Artificial strain fields have enabled the observation
of single photons from strain-induced arrays in WSe\(_2\)\(^9, 10\). It has been suggested that
the strain gradients locally modify the band gap, allowing the funnelling of excitons
toward isolated quantum emitters, which lie in deeper localized traps\(^10\). These results
point to the importance of understanding the nature and optical properties of point
defects in SL-WSe\(_2\).

It is interesting to ask why most successful SPE experiments in TMD have utilized
WSe\(_2\), rather than the more common TMD, MoS\(_2\), and why SL-WSe\(_2\) has been found
to have excellent optical quality compared to MoS\(_2\)\(^11\). These differences suggest that
the defect structure in WSe2 is fundamentally different from that in MoS2. Scanning
tunnelling microscopy (STM) and first principles density functional theory (DFT)
calculations have shown that sulphur vacancies Svac are the predominant point defects
in MoS2.12 The gap states in these sulphur vacancies are thought to give rise to poor
optical quality13. The chalcogen vacancy (Sevac) also has the lowest formation energy
among the intrinsic point defects in SL-WSe2.14 Recent electron-beam irradiation
experiments on SL-WSe2 have shown that Sevac gives a broad emission peak extending
to at least 0.2 eV below the A peak15. Many-electron GW-BSE calculations on Sevac in
SL-WSe216 and Svac in MoS217 also predict broad optical absorption spectra arising
from chalcogen vacancies. This implies that Sevac are not responsible for the localized
excitons ~45-100 meV below the A peak in SL-WSe23, 4, 5, 6, 7, 8. It has been suggested,
based on STM images, that W vacancies (Wvac) are the predominant point defects in
SL-WSe2, and are responsible for localized SPE18.

Using DFT calculations, we show that Sevac in SL-WSe2 is easily passivated by atomic
oxygen due to facile O2 dissociation at Sevac sites at room temperature. The resulting O
atoms passivate Sevac, giving an O-substituted Se vacancy (OSe), and forming
energetically favourable O interstitial defects (Oins) in addition to O adatoms (Oad).
Simulated STM images of these O defects agree well with our experimental STM
images and the aforementioned STM results18. The passivation of Sevac gap states
explains the superior optical quality and facilitates the observation of SPE from other defects.
Our first principles GW-Bethe-Salpeter-equation (GW-BSE) calculations show that Oins gives
rise to localized excitons ~50-100 meV below the free exciton peak, in good agreement with
the SPE previously observed in SL-WSe23, 4, 5, 6, 7, 8. OSe has no low energy excitons below
the A peak. Our high angle annular dark-field (HAADF) scanning transmission electron
microscopy (STEM) images showed that no W vacancies (Wvac) are present. STEM
images reveal SeW antisite vacancies, predicted to be the second-most stable intrinsic defect in typical Se-rich growth conditions. Our GW-BSE calculations for SeW show that like W\textsubscript{vac}\textsuperscript{16}, SeW gives rise to many sub-bandgap exciton peaks that are much lower in energy than the A peak. SeW and W\textsubscript{vac} defects may be possible sources of lower energy single photons, but cannot be responsible for the single photons previously observed in SL-WSe\textsubscript{2}.

**Results**

**Intrinsic point defects**

Fig. 1a shows the formation energy of intrinsic defects in SL-WSe\textsubscript{2} on graphite, computed using DFT (see methods). Subscripts ‘ad’, ‘vac’ and ‘int’ refer to adatoms, vacancies and interstitials, respectively. 2Se\textsubscript{vac} refers to a double Se vacancy at the same site and SeW refers to an antisite defect with Se substituting W. As Se and W adatom and interstitial defects can be removed by annealing, they are not our focus here. For both W-rich and Se-rich conditions, Se\textsubscript{vac} has the lowest formation energy (2.2-2.8 eV), while SeW, W\textsubscript{vac} and 2Se\textsubscript{vac} all have formation energies > 3 eV. Gap states are evident in the densities of states (DOS) of Se\textsubscript{vac}, SeW and W\textsubscript{vac} (Fig. 1b-d).
Figure 1. Intrinsic defects in SL-WSe2. (a) Formation energies of the intrinsic defects for SL-WSe2 on graphite. Solid lines denote vacancies, dashed lines substitutional (antisite) defects, dotted lines adatoms, and dotted-dashed lines intercalated atoms. (b-d) DOS of the 5×5 WSe2 supercell with intrinsic defects. The DOS plots are computed using the HSE06 hybrid exchange-correlation functional. Gray shading: DOS of perfect WSe2, aligned using the 1s core level of the W atoms furthest from the defect.

O2 dissociation at Se vacancies

In bulk semiconductors, it is common for point defects, especially vacancies, to be passivated by impurity atoms19. In 2D semiconductors where much of the material is exposed to the environment, it is even more important to consider the role of extrinsic defects. We have considered extrinsic point defects related to O, O2, H, H2 and C atoms. In this work, we focus on the most stable extrinsic point defects we found, namely, O bound to Sevac. The O-O bond length in O2-Sevac is > 20% larger than its gas phase value. Using the climbing image nudged elastic band method20, we compute an O2 dissociation barrier of 0.52 eV at Sevac (Fig. 2a). The reaction prefactor is computed using harmonic transition state theory21, giving a rate constant of ~10^5 counts/second at 300 K. This is consistent with the rule of thumb that a thermally activated process with barrier of ~30 kBT (0.7 eV) or below can take place at room temperature for typical attempt frequencies22. Zero-point energy corrections reduce the barrier height by 0.04 eV. Our results indicate that O2 can readily dissociate at Sevac at room temperature. In contrast, we compute a barrier of 0.94 eV for O2 dissociation at Svac in SL-MoS2, corresponding to a rate constant of only ~10^-2 counts/second at 300K. Fig. 2b-c shows that when O2 is adsorbed at Sevac, electrons are added to the antibonding orbital of O2 and depleted from the bonding orbital and nearby W atoms,
thus facilitating O\(_2\) dissociation. This net charge transfer to O\(_2\) (~0.6 e\(^{-}\)/atom) is in turn facilitated by the smaller work function of 2D WSe\(_2\) (4.69 eV) compared to MoS\(_2\) (5.06 eV). Based on the work functions, we expect the corresponding barriers for WS\(_2\) and MoSe\(_2\) to be larger than in WSe\(_2\) but smaller than in MoS\(_2\)^23. Indeed, oxygen-substitutional defects have also been identified in MoSe\(_2\) and WS\(_2\)^24. We note that quantitative prediction of energy barriers can be challenging for DFT. However, this does not affect our conclusion that O\(_2\) can dissociate easily at Se\(_{\text{vac}}\) sites in SL-WSe\(_2\), while the same cannot be said for S\(_{\text{vac}}\) in SL-MoS\(_2\). Other exchange-correlation functionals also give a barrier of at most 0.57 eV (see SI, Table S1).

Figure 2. O\(_2\) dissociative adsorption at the Se vacancy site and O-related defects in a 5 x 5 supercell. (a) O\(_2\) dissociation barrier. IS, TS and FS are initial, transition and final states, respectively. (b) Electron gain and (c) loss regions \(\Delta\rho\) for the IS, computed using 
\[
\Delta\rho = \rho_{\text{IS}} - \rho_{O_2} - \rho_{\text{Se}_{\text{vac}}}.
\]
(d-i) Atomic structures and DOS (HSE06) of O-related defects. (d-e)
In the final state (Fig. 2a), one O atom O1 takes the place of the missing Se (forming O$_{Se}$), while the other O2 binds to the neighbouring W atom. The adsorption energy $E_{ads}$ of O on Se$_{vac}$, referenced to atomic O is $\sim$ -7.1 eV. The next most stable binding sites for O are O$_{ins}$ (Fig. 2f; $E_{ads} = -2.9$ eV) and O$_{ad}$ (Fig. 2h; $E_{ads} = -2.4$ eV). The O atom O2 can move to these more stable sites with thermal annealing (e.g. Fig. S2). None of these defects have deep gap states (Fig. 2e, 2g, 2i). Since Se$_{vac}$ is the most abundant intrinsic point defect, and O$_2$ dissociation at Se$_{vac}$ is facile, we expect the highly stable O$_{Se}$ to be the most abundant point defect in 2D WSe$_2$.

**Experimental evidence**

Our low temperature STM measurements reveal the presence of three most commonly observed point defects (D$_1$, D$_2$ and D$_3$; Fig. 3a-c) in SL-WSe$_2$, grown via chemical vapour deposition (CVD) on graphite$^{25}$ and annealed in vacuum to $\sim$300 °C. The STM images for D$_1$ are similar to those in the literature$^{18}$. STM images simulated within the Tersoff-Hamann approximation$^{26}$ for O$_{Se}$, O$_{ins}$ and O$_{ad}$ compare well with the images of D$_1$, D$_2$ and D$_3$ (see Methods). Depending on the bias, the bright spots in the STM images for pristine WSe$_2$ can be attributed to Se sites or hollow sites (Fig. S4). The detailed patterns observed in the STM images for D$_1$, which are very different for different bias voltages, strongly support the conclusion that D$_1$ is O$_{Se}$. The unique pattern in D$_2$, together with the presence of O$_{Se}$, further supports the conclusion that D$_2$ is O$_{ins}$. We note that O$_{ins}$ and O$_{Se}$ (at the bottom Se site) have similar STM images for low bias voltages. However, the STM images differ for larger bias voltages, and a comparison
shows clearly that D$_2$ corresponds to O$_{\text{ins}}$ (Fig. S5). This is further supported by the different scanning tunnelling spectroscopy (STS) spectra for D$_1$ and D$_2$. None of the STM images simulated for the intrinsic defects (Fig. S6) match well with the experimental STM images for D$_1$ and D$_2$. Furthermore, no gap states are observed in the STS spectra (Fig. 3d-f), in contrast to the gap states predicted for intrinsic point defects. Interestingly, D$_1$ (O$_{\text{Se}}$) is observed to be the most abundant point defect (Fig. S3), as we predict for O$_{\text{Se}}$, while D$_2$ (O$_{\text{ins}}$) was also commonly observed. We were unable to locate any point defects with gap states in the STM/S experiments, consistent with the low density of such defects.

STEM measurements were also performed on SL-WSe$_2$ (see Methods). Analysis of the STEM image intensities (Fig. S7) led to the conclusion that the most abundant defect observed was Se$_{\text{vac}}$, while 2Se$_{\text{vac}}$ and Sew were also present (Fig. 4). As the atomic number of O atoms is much smaller than that of Se and W, and the HAADF STEM image intensity is approximately proportional to the square of the atomic number, O atoms are very challenging to detect above the background signal. Also, the knock-on damage threshold for the oxygen atoms may be below the 60 kV accelerating voltage used, which can also explain why O was not detected. No W$_{\text{vac}}$ were observed, consistent with typical Se-rich growth conditions.
Figure 3. Experimentally observed point defects. (a-c) Left: Experimental STM images for the dominant point defects (D₁, D₂ and D₃) observed in STM. Right: Simulated STM images of O_{Se}, O_{ins} and O_{ad}. Voltages on the left are tip bias voltages (negative biases correspond to unoccupied states and vice versa). Voltages on the right are relative to E_F in the calculation, chosen to approximate the energy ranges of states contributing to the measured STM current. Atomic positions are shown in a and b. (Red: O; Blue: W; Green: Se). (d-f) Averaged STS spectra on (red) and away from (> 2nm, black) the defects.
Figure 4. HAADF STEM images (60 kV accelerating voltage). The two images are for the exact same area. Se\textsubscript{w} (red) and 2Se\textsubscript{vac} (green) are marked in a, while Se\textsubscript{vac} (orange) are marked in the top right of b. O atoms cannot be distinguished due to the low knock-on damage threshold and much smaller atomic number of oxygen compared to Se and W.

**Optical properties of point defects**

Point defects are a likely source of the localized excitons responsible for SPE experimentally observed in SL-WSe\textsubscript{2}. We use state-of-the-art first principles GW-BSE calculations to explore the implications of these point defects on the optical response of SL-WSe\textsubscript{2}. We focus here on O\textsubscript{Se}, O\textsubscript{ins}, and Se\textsubscript{w}. The optical properties of Se\textsubscript{vac} and W\textsubscript{vac} have been studied in the literature\textsuperscript{16}. The GW-BSE calculations account for electron self-energy effects in the quasiparticle spectra as well as electron-hole interactions in the excitons. State-of-the-art k-point interpolation methods are used to obtain good convergence\textsuperscript{17,27}. 4 x 4 supercells are considered for these calculations, while optical properties are also computed in the random phase approximation (RPA) for 7 x 7 supercells as a comparison. RPA calculations for 4 x 4 cells are also
performed with and without spin orbit coupling (SOC) effects to estimate the effects of SOC on the optical spectra.

Figure 5. Electronic and optical properties for the O_{ms} point defect in a 4 x 4 supercell of SL-WSe\textsubscript{2}. (a) GW band structure, (b) GW-BSE optical absorption spectrum, (c) DFT band structure with spin-orbit coupling (SOC) effects (the colour scale depicts the projection of the spin along the z axis), (d) RPA spectra with and without SOC effects. Note that in (b) the broadening is reduced into 0.002 eV with vertical axis in log-scale to emphasize the LX\textsubscript{1} peak. The dashed line in (b) is the GW-BSE spectrum for pristine SL-WSe\textsubscript{2} with no defects. The blue line represents the optical spectrum computed in the independent particle approximation (no electron-hole interactions) using the GW eigenvalues. In (d), the RPA spectrum without SOC was shifted by +0.87 eV to align the optical onset with the GW-BSE spectrum without electron-hole
interactions (due to the difference in single-particle energies between the two calculations). The RPA SOC spectrum was shifted by the same amount for comparison.

We first focus on the O$_{ins}$ defect (Fig. 5). Interestingly, there is a low energy exciton (LX$_1$; Fig. 5b) at 1.78 eV, 50 meV below the energy of the free exciton A peak in pristine WSe$_2$. Analysis of the exciton wavefunctions (Table S3) shows that the A peak in the defect cell is at 1.97 eV (Fig. 5b), and that LX$_2$ and LX$_3$ are also defect-related excitons ~100 meV below the A peak in the defect cell. The difference in energy between LX and A peaks lies in the same range as that experimentally observed in SL-WSe$_2$ (~45-100 meV). This indicates that the O$_{ins}$ point defect is a likely source for the SPE observed in SL-WSe$_2$. In particular, as we discuss below, no other point defects give similar spectra.

In the limit of low defect density, we should take the free energy exciton to be that in the pristine case. This implies that the LX$_1$ peak is the most likely to be related to the localized excitons in experiment. LX$_1$ primarily results from a combination of the bulk VBM-1 state and defect CBM state at the K point (Table S3; Fig. S8; Fig. 5a). The localized nature of the defect state supports the emission of single photons, while the involvement of the bulk state is consistent with the valley polarization of single photons observed in Reference 3. Other LX excitons are related to transitions between the VBM-1/VBM-2 states and CBM. From Fig. 5b, we note that electron-hole interactions are important for reducing the optical onset and creating separate energy peaks (LX versus A), pointing to the importance of excitonic effects in this defect system.
Figure 6. Optical absorption spectra for OSe and SeW point defects, each in a 4 x 4 supercell of SL-WSe$_2$. (a) GW-BSE and (b) RPA spectra for OSe, (c) GW-BSE and (d) RPA spectra for SeW. The RPA spectra in (b) and (d) are shifted by +0.92 and +0.77 eV, respectively, to match the GW-BSE spectra without electron-hole interactions. Labels A in (c) and (d) mark the free exciton A peak energy positions in the respective spectra. Plots of (a) and (c) with a log-scale and smaller broadening are shown in Fig. S9.

In Fig. 6, we show the optical absorption spectra computed for OSe and SeW defects. For the OSe defect system, there are no lower energy excitons below the first prominent peak (corresponding to the free exciton A peak). The optical band gap is narrowed to 1.76 eV, 60 meV lower than that of pristine SL-WSe$_2$. For the SeW defect, the deep defect states (Fig. S11) result in a large number of bound excitonic transition
levels below the A peak, spanning a wide energy range (~1.3 eV), down to ~0.3 eV (Fig. 6c). This implies that SeW defects cannot be responsible for the SPE previously observed in SL-WSe2. However, depending on the exciton dynamics in this system, our results indicate that SeW point defects are promising for SPE in the infrared and near-infrared spectral range.

It is not possible to include SOC effects explicitly for such large supercells in GW-BSE calculations. Including SOC effects perturbatively for the pristine WSe2 system28, we obtain an A peak at 1.6 eV and a B peak at 2.0 eV, close to the experimentally measured 1.75 eV and 2.20 eV29. The DFT band structure of the defect supercells, including SOC effects (Fig. 5c; Fig. S10-11), suggest that spin is not a good quantum number for states near the VBM and CBM. We therefore estimate the effects of SOC by comparing DFT RPA spectra (independent particle approximation) with and without SOC (Fig. 5d, 6b, 6d). There is no obvious change in the optical activity of the transitions and the two spectra are in general very similar, except for a narrowing of the optical onset by ~0.2 eV because of the smaller DFT band gap when SOC is included. SOC effects may also explain why multiple localised exciton peaks are observed in experiment.

In Fig. S12, we compare the RPA spectra for 4 x 4 and 7 x 7 supercells. For Oins and OSe, the RPA spectra for 4 x 4 and 7 x 7 supercells are very similar, apart from a small shift in energy. For Sew, the 7 x 7 supercell has fewer peaks in the RPA spectrum, but these peaks are still deep in the band gap and thus do not change our qualitative results that Sew is likely to emit in the infrared range.

**Discussion**
We have presented a detailed theoretical and experimental study of the nature of point defects in SL-WSe$_2$. Our DFT and STM results show that O$_{Se}$ is the most abundant defect in 2D WSe$_2$, passivating the gap states. This explains the superior optical quality of WSe$_2$, and facilitates the observation of SPE from localized excitons. The origin of quantum emitters in SL-WSe$_2$ is unknown. The band gap of SL-WSe$_2$ can be modulated by strain and defects, thus enabling the funnelling of excitons to particular regions in space. For photons to be emitted one at a time, the excitons should involve localized states$^{2,10}$. Therefore, together with strain gradients, point defects are important to give rise to highly localized excitons. We have used state-of-the-art first principles calculations to predict the optical properties of O$_{Se}$, O$_{ins}$ and Se$_{W}$ point defects, that have been observed in experiment. O$_{ins}$ gives localized excitons in an energy range that is in good agreement with previous observations of SPE in SL-WSe$_2$ ($\sim$45-100 meV below the A peak)$^{3,4,5,6,7,8}$ No other point defect gives similar agreement. The O$_{Se}$ defect does not give rise to low energy excitons, while the deep gap states in Se$_{W}$ defect gives much lower energy excitons, similar to W$_{vac}^{16}$. Se$_{vac}$ defects should not normally be present, but even if they are, they result in a broad emission peak 0.2-0.3 eV below the A peak$^{15}$. This strongly suggests that O$_{ins}$ defects are responsible for single photon emission previously observed in SL-WSe$_2$. In contrast to WSe$_2$, the O$_2$ dissociation energy at chalcogen vacancies in MoS$_2$ is rather high, and this can explain why WSe$_2$, rather than MoS$_2$, has been found experimentally to host quantum emitters. Taken together, our results suggest ways to create quantum emitters in other semiconducting TMDs, e.g. through controlled reaction with O$_2^{30}$ and point experimentalists toward other energy ranges in which single photons may be emitted in the TMDs.

**Methods**
Except for calculations on optical properties, all our DFT calculations are performed using the VASP code\textsuperscript{31,32} using PAW potentials. We use the PBE exchange-correlation functional\textsuperscript{33} with Grimme’s D2\textsuperscript{34} correction for van der Waals (vdW) interactions for all calculations except the density of states (DOS) plots which were performed with the hybrid HSE06\textsuperscript{35} exchange-correlation functional. Spin polarization is included for the defect structures and for oxygen.

STM images were simulated in the Tersoff-Hamann approximation.\textsuperscript{26} The Tersoff-Hamann approximation predicts STM images\textsuperscript{12} for $S_{\text{vac}}$ in SL-MoS$_2$ in good agreement with experiment, and with more sophisticated calculations including tip effects\textsuperscript{36}. Besides the images obtained with the PBE exchange-correlation functional (Fig. 3), we have also simulated images using the HSE06\textsuperscript{35} functional (Fig. S13), which also agree well with experiment.

Our GW-BSE calculations are performed with Quantum-ESPRESSO\textsuperscript{37} and BerkeleyGW\textsuperscript{38} software. PBE optimized norm-conserving Vanderbilt (ONCV) pseudopotentials\textsuperscript{39} were used, with a kinetic energy cutoff of 60 Ry. W semicore 5s, 5p and 5d states were included as valence electrons. Defective 4x4 supercells were fully relaxed with the lattice parameters fixed at 4 times of the primitive WSe$_2$ cell. We performed one-shot G0W0 calculations with a dielectric matrix cutoff of 15 Ry, slab Coulomb truncation\textsuperscript{40}, the Hybertsen-Louie generalized plasmon pole model\textsuperscript{41}, and the static remainder method to speed up convergence\textsuperscript{42}. The reciprocal space was sampled using non-uniform neck subsampling (NNS) in GW and cluster sampling interpolation (CSI) in BSE\textsuperscript{27}. Using these methods, we converged the GW quasiparticle energies in the primitive WSe$_2$ cell using a 15x15x1 q-mesh and 520 bands, and converged the BSE spectrum using a 72x72x1 fine-mesh and the CSI scheme with sub-factor 3. In the 4x4 supercells with defects, we used a 4x4x1 q-mesh.
and 1500 bands to compute the GW eigenvalues, and for the BSE part, we calculated the kernel matrix elements with a 6x6x1 k-mesh, and interpolated them to a 18x18x1 fine mesh. In addition, we used the CSI method with sub-factor 3 to generate an even finer effective k-mesh. BSE equation is solved by direct diagonalization within the Tamm-Dancoff approximation (TDA), including bands with energy at least 0.5 eV beyond the VBM and CBM.

RPA calculations were performed with Yambo.43

STEM measurements were performed on SL-WSe2, CVD grown on sapphire25 and transferred to a TEM grid for measurement. A 60 kV accelerating voltage was used.

Further details on methods used are provided in the SI.

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Author contributions
YJZ did the DFT calculations analysing defects, YC performed the GW-BSE and RPA calculations, and PET performed the RPA calculation with 7x7 cells. YJZ performed the STM experiments with supervision from YLH and ATSW. PKG performed the STEM experiments with supervision from SJP. YJZ, YLH and PKG analysed the experimental data. MYL and LJL provided the samples. SYQ supervised the theoretical calculations and directed the project. SYQ, YJZ and YC wrote the manuscript with input from all authors.

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Supplementary Information for:

The origin of single photon emission in 2D WSe₂

Yu Jie Zheng¹,², †, Yifeng Chen², †, Yu Li Huang¹,³, Pranjal Kumar Gogoi¹, Ming Yang Li⁴, Lain-Jong Li⁴, Paolo E. Trevisanutto², Qixing Wang¹, Stephen J Pennycook⁵,*, Andrew Thye Shen Wee¹,², *, Su Ying Quek¹,², *

¹Department of Physics, National University of Singapore, 2 Science Drive 3, 117551, Singapore

²Centre for Advanced 2D Materials, National University of Singapore, Block S14, Level 6, 6 Science Drive 2, 117546, Singapore

³Institute of Materials Research & Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, 138634, Singapore

⁴Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

⁵Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575

†: These authors contributed equally to this work.
Corresponding Authors *: phyqsy@nus.edu.sg (theory); phyweets@nus.edu.sg (STM); msepsj@nus.edu.sg (STEM)
METHODS
1. Density Functional Theory (DFT) calculations  3
2. Chemical Vapor Deposition (CVD)  4
3. Scanning tunneling microscopy/spectroscopy (STM/S)  4
4. Scanning Transmission Electron Microscopy (STEM)  5

FIGURES
FIG. S1. Atomic structure and DOS for the final state in Figure 2a of the main text.  6
FIG. S2. O$_2$ dissociative adsorption at the Se vacancy site.  7
FIG. S3. STM images of point defects in SL-WSe$_2$/graphite.  8
FIG. S4. Perfect SL-WSe$_2$ on graphite.  9
FIG. S5. STM images for D$_2$, compared with simulated STM images for O$_{\text{ins}}$ and O$_{\text{Se-down}}$ (O substituting the bottom Se atom).  10
FIG. S6. Simulated STM images of the intrinsic defects in SL-WSe$_2$ on graphite.  11
FIG. S7. HAADF STEM image at 60 kV accelerating voltage together with intensity analysis.  12
FIG. S8. Charge density plots for DFT eigenfunctions at the K point, in the 4 x 4 supercell with O$_{\text{ins}}$.  13
FIG S9. GW-BSE optical absorption spectra for 4x4 supercell with (a) O$_{\text{Se}}$ and (b) Sew antisite defect with smaller 0.002 eV broadening in a log-scale plot.  14
FIG S10: (a) GW and (b) DFT-SOC band structure with $m_z$ projection for 4x4 supercell with O$_{\text{Se}}$ defect.  14
FIG S11: (a) GW and (b) DFT-SOC band structure with $m_z$ projection for 4x4 supercell with Sew defect.  14
Figure S12. RPA spectra without SOC for 7x7 supercell of (a) O$_{\text{ins}}$, (b) O$_{\text{Se}}$, and (c) Sew antisite defect.  15
Figure S13: STM images simulated with HSE06 functional.  16

TABLES:
Table S1. Energy barrier for dissociation of O$_2$ on Se$_{\text{vac}}$ in WSe$_2$, computed for different exchange-correlation functionals.  5
Table S2. Binding energies ($E_b$) of the O atoms in the final state.  7
Table S3. Analysis of exciton wavefunctions.  13
METHODS

1. Density Functional Theory (DFT) calculations

**Electronic Properties of Defects**

Except for the calculations for optical properties, the density functional theory (DFT) calculations in this manuscript were performed with the VASP code [1,2] using PAW potentials and a kinetic energy cutoff of 400 eV. We use the PBE exchange-correlation functional[3] with Grimme’s D2[4] correction for van der Waals (vdW) interactions for all calculations except the density of states (DOS) plots which were performed with the hybrid HSE06[5] exchange-correlation functional. Spin polarization is included for the defect structures and for oxygen. Geometry optimization is performed with a force convergence criteria of 0.01 eV/Å for single layer (SL)-WSe₂, and 0.05 eV/Å for SL-WSe₂ supported on graphite. The lattice constant is fixed to that optimized for the pristine WSe₂ layer, which compares well to experimental values. The total energy of bulk WSe₂ is converged for the chosen energy cutoff, as well as with a Monkhorst Pack k-grid sampling of 10 × 10 × 4 in the bulk WSe₂ unit cell. SL-WSe₂ on graphite was modeled using 3 layers of graphite, with a 3 × 3 WSe₂ supercell on top of a 4 × 4 supercell of graphite and 13 Å of vacuum. In this supercell, the strain on WSe₂ was 0.61 % and the strain on graphite was -0.65 %. Defects in SL-WSe₂ on graphite were studied using a 2×√3R30° supercell of the WSe₂/graphite supercell described above. In these defect supercells, we used a k-mesh of 2 × 2 × 1 for geometry optimization and 4 × 4 × 1 for DOS calculations. For defects in isolated WSe₂, we used a 5 × 5 supercell, with a 2 × 2 k-mesh for geometry optimization and a 6 × 6 k-mesh for DOS calculations.

For the computation of dissociation barriers and rate constants, 5×5 supercells with >15 Å vacuum were used, with a Monkhorst-Pack k-mesh of 2×2×1 and a force convergence criterion of 0.01 eV/Å. The dissociation barrier was computed using the climbing image nudged elastic band (ci-NEB) method [6]. The prefactor of the reaction was estimated within harmonic transition state theory (HTST) [7,8], and is given by \[ A = \frac{\prod_{i=1}^{N} \nu_{i}^{IS}}{\prod_{i=1}^{N-1} \nu_{i}^{TS}} \], where N is the number of free atoms, \( \nu_{i}^{IS} \) and \( \nu_{i}^{TS} \) are stable (real valued) normal mode frequencies at the initial states (IS) and transition states (TS) or saddle point. At the transition state, exactly one of the vibrational modes has an imaginary frequency. From the prefactor \( A \), the rate constant \( k \) is obtained by \[ k = A \exp \left( -\frac{E^{TS} - E^{IS}}{k_{B}T} \right) \]. \( E^{IS} \) and \( E^{TS} \) are the energies at the initial and transition states. \( k_{B} \) and \( T \) are the Boltzmann’s constant and temperature, respectively.

Besides using the PBE-D2 functional as described in the main text, we have also computed the O₂ dissociation barriers using the RPBE functional[9] with and without Grimme’s D3 dispersion correction,[10] and the BEEF-vdW functional.[11] The RPBE functional, when applied to dissociative adsorption of O₂ on Cu surfaces, gave
reasonable agreement with experiment,[12] while the BEEF-vdW functional performed
good compared to an experimental benchmark database of molecular dissociation
barriers on surfaces.[13] The results are shown in Table S1.

DFT band structures with spin orbit coupling (SOC) were also computed using VASP.

**Random Phase Approximation (RPA) calculations**

RPA calculations were performed with Yambo[14] using a damping parameter of 0.01
eV. RPA with SOC calculations were performed with spinor wavefunctions using fully
relativistic ONCV pseudopotentials. For 4x4 supercells, the response function has a
dimension in reciprocal space of 1000 mHa. However, for \( 7 \times 7 \) supercells, the
corresponding dimension is \(~0.5 \) mHa due to the large computational expense.

2. **Chemical Vapor Deposition (CVD)**

Monolayer WSe\(_2\) was grown directly on graphite and on sapphire substrates by chemical
vapor deposition (CVD) as reported in Ref. [15]. In brief, high purity WO\(_3\) and Se powders are
used as precursors. WO\(_3\) powders were placed in a ceramic boat at the center of a furnace and
Se powders were placed at the upstream side, while the graphite or sapphire substrate was
positioned in the downstream side next to the WO\(_3\) powders. Ar was used as carrier gas to carry
the evaporated Se and WO\(_3\) to the target substrates for reaction. H\(_2\) was added as a reducing
agent. STM and STEM confirmed that the samples used were monolayer in thickness.

3. **Scanning tunneling microscopy/spectroscopy (STM/S)**

STM/S measurements were performed in a custom-built multi-chamber system housing an
Omicron LT-STM operating at ~77 K under ultrahigh vacuum conditions (10\(^{-10}\) mbar). All
STM images were recorded in constant current mode with tunneling current in the range 50-
100 pA. Differential conductance dI/dV or STS were acquired by a lock-in amplifier with a
sinusoidal modulation of 40 mV at 625 Hz. Note that the bias voltage (\(V_{\text{tip}}\)) is applied on the
STM tip with respect to the sample, hence negative values correspond to empty states and
positive values correspond to filled states. Each STS curve was obtained by averaging hundreds
of individual spectra acquired. An electrochemically etched tungsten tip was used in all
measurements. Before STM investigations, the *ex-situ* grown sample was degassed at ~300 °C
overnight to remove adsorbates (*e.g.*, O\(_2\), H\(_2\)O, *etc.*) physisorbed during exposure in ambient
conditions.
4. Scanning Transmission Electron Microscopy (STEM)

Transfer to TEM grid:
At first, the WSe₂/sapphire sample surface was spin-coated with poly(methyl methacrylate) (PMMA, A4, 950 K in anisole, MicroChem) at 4000 rpm for 60 second. After curing the spin-coated sample at 100° C for 10 min, the edges of the sample were scratched, so that the etching agent can easily reach the WSe₂-sapphire interface. The sample was then floated on NaOH (3M) etching solution to separate the PMMA coated WSe₂ film from the sapphire substrate. After separation, the floating film was transferred to DI water beakers a few times consecutively and later fetched using a quantifoil copper TEM grid. The TEM grid with PMMA-coated WSe₂ film was thereafter heated at 100° C for 5 min to get better adhesion and to remove water. The PMMA coating was washed off finally, using acetone and IPA. This transfer process was carried out inside a class 1000 cleanroom in Singapore Synchrotron Light Source (SSLS) situated at the National University of Singapore (NUS) campus.

Scanning Transmission Electron Microscopy:
Aberration-corrected scanning transmission electron microscopy (STEM) images were taken at 60 kV accelerating voltage using the JEOL ARM200 F installed inside SSLS, NUS. The microscope, with 80 pm resolution at 200 kV and demonstrated information transfer of 95 pm at 40 kV, is capable of high-resolution imaging to reveal the atomic structure and defects. The lower accelerating voltage of 60 kV used here for WSe₂ is much below the knock-on damage threshold of Se and W atoms in WSe₂, and hence it ensures negligible beam-damage. High-angle annular dark-field (HAADF) image intensities depend on the atomic number of the corresponding atoms in the sample. All the images reported here were taken with the HAADF detector with the collection angle range of 68-280 mrad. The convergence angle of the probe beam was about 30 mrad.
Table S1. Energy barrier for dissociation of O$_2$ on Se$_{\text{vac}}$ in WSe$_2$, computed for different exchange-correlation functionals.

|          | PBE-D2          | PBE-D2 (with zero point correction) | RPBE | RPBE-D3 | BEEF-vdW$^1$ |
|----------|-----------------|------------------------------------|------|---------|--------------|
| Barrier (eV) | 0.52            | 0.48                               | 0.54 | 0.57    | 0.51         |

$^1$. For BEEF-vdW, the number in the table is obtained from structures where the lattice constant is fixed to that of PBE-D2, which is closer to experiment. Using the lattice constant optimized with BEEF-vdW (overestimated by ~3.5%), we obtain a much smaller energy barrier of 0.13 eV.

FIG. S1. Atomic structure and DOS for the final state in Figure 2a of the main text. (a) Top view of atomic structure (Blue: W, Green: Se, Red: O), (b) DOS of final state, (c) PDOS on the O atoms which are marked in (a). Gray shading represents the DOS of perfect WSe$_2$, aligned using the 1s levels of W atoms furthest from the defect.
Table S2. Binding energies \( (E_b) \) in eV of the O atoms in the final state. \( E_b = E_{2O} - E_{1O} - \mu_O \), where \( E_{2O} \) is the total energy of the final state in Figure 2a, \( E_{1O} \) is the total energy after the specified O atom is removed, and \( \mu_O \) is half of the total energy of O\(_2\), and for the number in brackets, \( \mu_O \) is the energy of atomic O. Spin polarization is included. We see that the O1 atom is much more strongly bound than O2.

|   | O1    | O2    |
|---|-------|-------|
| \( E_b \) | -4.2 (-6.8) | 0.3 (-2.3) |

FIG. S2. (a) O\(_2\) dissociative adsorption at the Se vacancy site and diffusion of oxygen atom to (a) O\(_{ad}\); (b) Energy barrier for O atom to diffuse from O\(_{ad}\) to O\(_{ins}\). The energy barrier from O\(_{ad}\) to O\(_{ins}\) is 1.5 eV, smaller than the binding energy of O atoms (relative to atomic O) at the different binding sites.
FIG. S3. STM images of point defects in SL-WSe$_2$/graphite ($V_{\text{tip}} = 1\text{V}$). D1 (black arrow), D2 (red arrow) and D3 (green arrow) correspond to O$_{\text{Se}}$, O$_{\text{ins}}$ and O$_{\text{ad}}$ respectively. Lower left corner inset gives the estimated densities of the defects.
FIG. S4. Perfect SL-WSe$_2$ on graphite. a) Atomic structure. (Blue: W; Green: Se; Gray: C) b) PDOS (PBE) of WSe$_2$ on graphite reveals a 1.55 eV band gap. c) STS spectrum reveals a 2.02 eV bandgap for SL-WSe$_2$ ($V_{\text{Tip}}=1.3$ V, 68.5 pA) on graphite with slight p-type doping characteristic, similar to previous reports.[16] d) Simulated STM images at different bias voltage (values in parenthesis referenced to the band edges) with atoms overlain in the images (Blue spots: W, Green spots: Se). Energy ranges chosen for the simulation approximate those in the experiment. e) Bias dependent experimental STM images of SL-WSe$_2$ on graphite (values in parenthesis referenced to band edges).
FIG. S5. STM images for D₂, compared with simulated STM images for O_{ins} and O_{Se-down} (O substituting the bottom Se atom)
FIG. S6. Simulated STM images of the intrinsic defects in SL-WSe$_2$ on graphite. The energy ranges are chosen to probe occupied and unoccupied states that are 0.3 eV away from the band edges. Atomic positions are overlain on the images. Blue: W, Green: Se. Se$_1$vac and Se$_2$vac refer to single Se vacancies with the missing Se being in the top and bottom layer, respectively.
FIG. S7. HAADF STEM image at 60 kV accelerating voltage together with intensity analysis. (a) Raw experimental HAADF STEM image presented in the main text Fig. 4 (g) and (h) (no overlaid atoms now) is shown. (b) Simulated HAADF STEM image and intensity profile, obtained using QSTEM simulation package with input parameters same as in experiments, are shown for the representative case of a region with one Se$_{\text{vac}}$. The brighter spots are due to W atoms and the lesser intensity ones are due to two Se atoms at the Se site. One Se$_{\text{vac}}$ is in the simulated image as can be seen in the line profile. The Se$_{\text{vac}}$ can be easily distinguished both in the simulated image as well in the line profile due to its reduced intensity. (c) The same experimental HAADF STEM image as in (a) is shown now with line profiles indicated. The red line profile captures a Se$_{\text{vac}}$, the blue line profile captures a 2Se$_{\text{vac}}$, and the green line profile captures a Se$_{\text{w}}$. (d) The corresponding intensity line profiles are plotted for the regions indicated in (c). These experimental line profile intensities (taking the background also into consideration) are used to distinguish the nature of defects by comparing them with corresponding simulated image intensities quantitatively.
FIG. S8. Charge density plots for DFT eigenfunctions at the K point, in the 4 x 4 supercell with O_{ins}. The isovalue is set to 10% of the maximum of the respective charge distribution, except for VBM, which is set to 1% for better visualization.

| LX1: 1.783 eV | CBM    | CBM+1  | CBM+2  | LX2: 1.860 eV | CBM    | CBM+1  | CBM+2  |
|--------------|--------|--------|--------|--------------|--------|--------|--------|
| VBM          | 0.00006| 0.00000| 0.00000| VBM          | 0.00002| 0.00001| 0.00000|
| VBM-1        | 0.88401| 0.04781| 0.00009| VBM-1        | 0.41199| 0.11755| 0.00366|
| VBM-2        | 0.02064| 0.00593| 0.00002| VBM-2        | 0.40391| 0.00617| 0.00269|

| LX3: 1.880 eV | CBM    | CBM+1  | CBM+2  | A: 1.978 eV | CBM    | CBM+1  | CBM+2  |
|--------------|--------|--------|--------|------------|--------|--------|--------|
| VBM          | 0.00065| 0.00002| 0.00000| VBM        | 0.00036| 0.00015| 0.00002|
| VBM-1        | 0.66412| 0.08961| 0.00271| VBM-1      | 0.23457| 0.42535| 0.01096|
| VBM-2        | 0.17760| 0.00832| 0.00434| VBM-2      | 0.19933| 0.02762| 0.01315|

Table S3: Analysis of exciton wavefunction for first few bright exciton states in the 4x4 supercell with O_{ins}. The numbers shown are $\sum_{k} A^S_{vck}$ for each combination of valence state $v$ and conduction state $c$, where the exciton wavefunction is given as $\Psi^S(r_v,r_c) = \sum_{vck} A^S_{vck} \psi_v(r_v) \psi_c(r_c)$. Major contributing entries are highlighted in red.
FIG S9. GW-BSE optical absorption spectra for 4x4 supercell with (a) OSe and (b) Sew anti-site defect with smaller 0.002 eV broadening in a log-scale plot.

FIG S10: (a) GW and (b) DFT-SOC band structure with m_z projection for 4x4 supercell with OSe defect.

FIG S11: (a) GW and (b) DFT-SOC band structure with m_z projection for 4x4 supercell with Sew defect.
Figure S12. RPA spectra without SOC for 7×7 supercell of (a) O_{ins}, (b) O_{Se}, and (c) Se_{W} anti-site defect, in comparison with the corresponding 4×4 supercell result. The 0.072 eV red shifted 4×4 spectrum in (a) is to account for the DFT gap size difference between 4×4 and 7×7 supercell systems. The fact that fewer peaks are present in the 7×7 supercells may be related to the limited number of valence and conduction bands in these calculations.
FIG. S13. STM images simulated with HSE06 functional. Left: Experimental STM (Omicron LT-STM operating at ~77 K and 10^{-10} mbar) images for (a) D1 and (b) D2. Right: Simulated STM images of (a) OSe and (b) O_{ins} using the HSE06 exchange-correlation functional. The atoms are overlain in the images for D1 and D2 defects. (Red: O; Blue: W; Green: Se).

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