

Atomic Defects and Doping of Monolayer NbSe₂

Lan Nguyen, Hannu-Pekka Komsa, Ekaterina Khestanova, Reza J. Kashtiban, Jonathan J.P. Peters, Sean Lawlor, Ana M. Sanchez, Jeremy Sloan, Roman V. Gorbachev, Irina V. Grigorieva, Arkady V. Krasheninnikov, Sarah J. Haigh

Supplementary information

Electron diffraction thickness determination

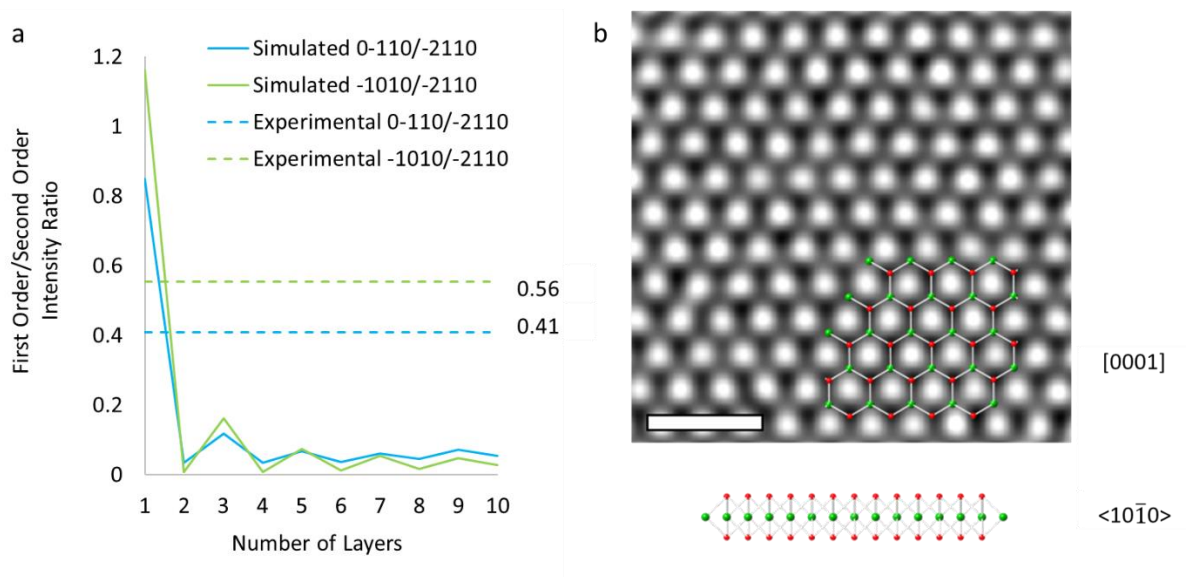


Fig. S1: (a) Line graph showing simulated and experimental intensity ratios of first and second order diffraction peaks as a function of thickness. Ratios obtained from (1d) for two sets of first order spots are: 0.56 and 0.41 (for $\bar{1}010$ and $0\bar{1}10$ respectively) which lies in between the simulated ratio for monolayer and multi-layered NbSe₂. (b) Atomic resolution of monolayer NbSe₂ [0001] (scale bar: 1nm). We do not find that the presence of encapsulating graphene sheets had any significant effect on these intensity ratios.

Focal Series thickness determination

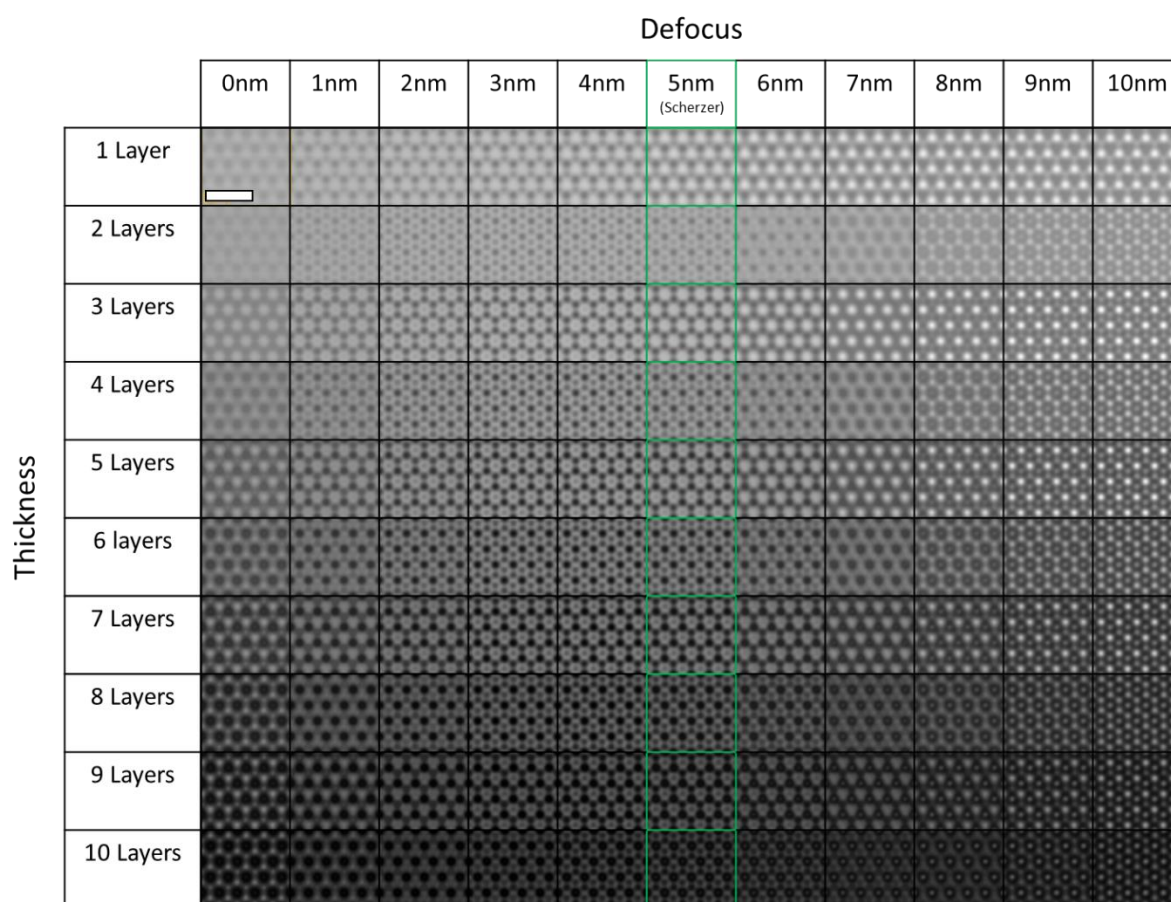


Fig. S2: Multislice focal series simulations for different thicknesses of NbSe₂. Comparison to experimental images shows that at Scherzer defocus, monolayer NbSe₂ matches most closely, confirming the observation of monolayers (scale bar: 1nm). JEMS simulation parameters: JEOL 2100F Cs Microscope; accelerating voltage: 80kV; C_c: 1.2mm; C_s: -0.005mm; C₅: 10mm; defocus spread: 6nm and energy spread: 0.81eV.

Image processing to reveal the nature of point defects

Raw images were Fourier filtered so that 1st and 2nd order graphene diffraction spots were removed using a low pass filter, to remove any image contributions of the graphene lattice. Image stacks were then aligned using a normalised correlation co-efficient matching method with the template being the whole image area in addition to subpixel registration. To highlight defect dynamics, a 2D Gaussian filter was further applied to all images in the stack with a 1σ magnitude in both x/y directions. Defective areas were measured with polygons and were defined by unordered clusters of defects which could not be categorised. Image brightness and contrast have been adjusted for clarity in figures.

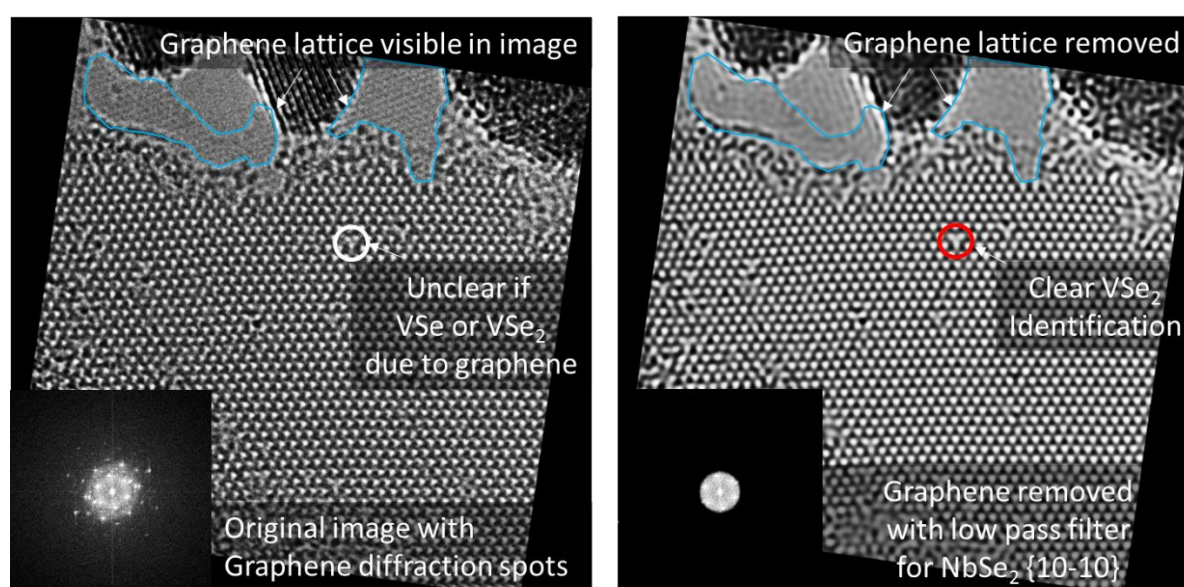


Fig. S3: Low-pass Fourier filtering around NbSe₂ {10 $\bar{1}$ 0} to remove contributions of graphene sheets. Comparison of image before and after low-pass filtering, showing the removal of graphene diffraction spots in the FFT removes graphene contributions from image. This also allows for the clear distinction of between defects such as V_{Se} and V_{Se2}.

The presence of a vacancy defect in the graphene sheet could in theory have a small effect on the intensity of an individual NbSe₂ defect in the filtered image. However, the two graphene sheets are incommensurate both with each other and with the NbSe₂ lattice so the precise contrast change will vary on a case by case basis and we assess this to be less than the Poisson noise of the images.

DFT analysis of Se vacancy clustering



Fig. S4: Vacancy clustering grouped by type of cluster. The circles on the atomic structure illustrate where the vacancies are created. Red and cyan circled atoms denote vacancies in bottom and top layers, respectively. Next to them, the first number denotes the number of missing Se atoms (N), second the formation energies with respect to the same number of isolated vacancies, and the third the same divided by N. The lowest energy configuration for defect clustering found from DFT calculations is for defects to cluster at 2nd nearest neighbour sites. However, our experimental images do not show such extended defects; the majority of defects are located further apart. This suggests that the presence of one defect does not increase the likelihood of other defects forming in the same region of the crystal.

Image intensity profile simulation for substitutional atoms in an Se monovacancy site

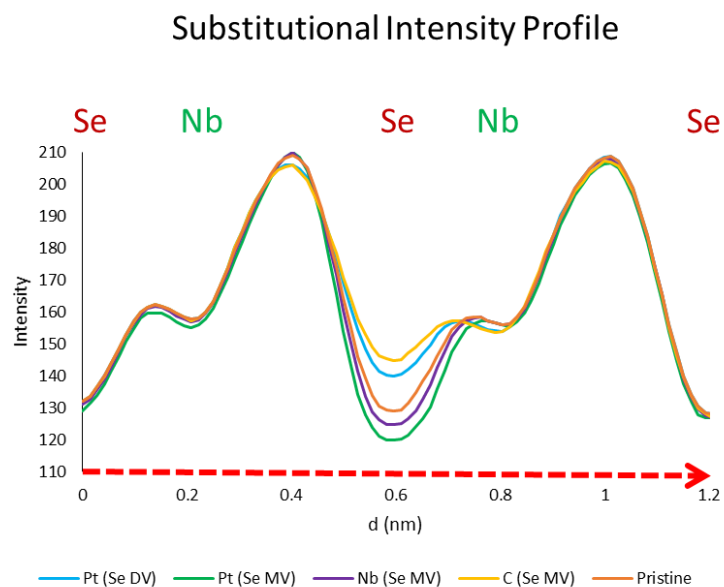


Fig. S5: Intensity profile from multislice simulations of substitutional atoms in a Se monovacancy site.

Stability and configuration of C substituted Se Vacancies

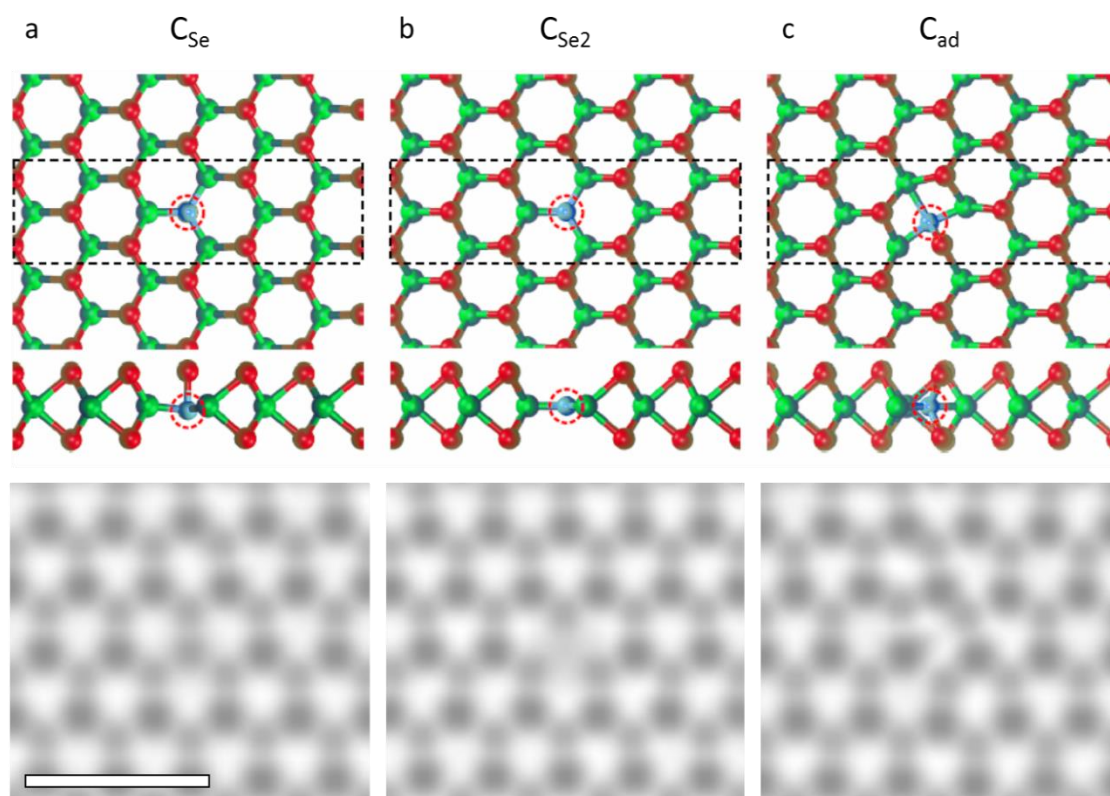


Fig. S6: Carbon defects in $NbSe_2$ and respective multislice simulations. Carbon atoms in the relaxed structures are 'pulled' towards the centre, at the same 'height' as Nb atoms (scale bar: 1nm)

Geometric Phase Analysis (GPA)

GPA was performed using the in house developed Strain++ program [<http://jippeters.github.io/Strainpp/>]. Before performing the analysis, a Hann window was applied to each image to remove edge effects in the Fourier transforms. The selected g-vectors were refined by minimizing the gradient of the phase taken from an area with zero strain. To select the Fourier components, masks with a Gaussian profile were used with a size large enough to maximise resolution without including significant noise effects (here a standard deviation of $\sim \frac{1}{6} \mathbf{g}_{\min}$ is used, where $\mathbf{g}_{\min}$ is the smallest g-vector). The same two g-vectors were selected for every analysis (shown in fig S4).

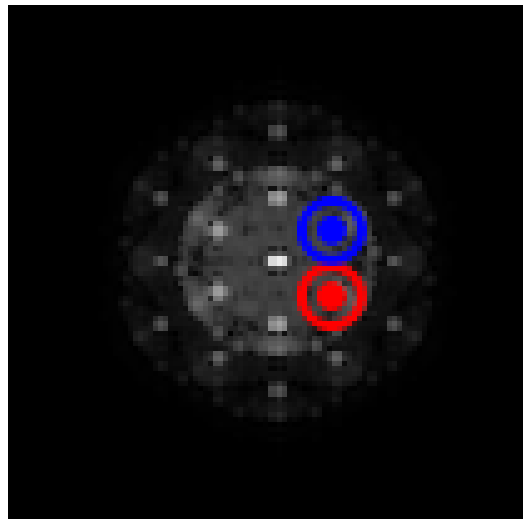


Fig. S7: G-vectors used for GPA strain analysis of point defects in graphene.

Small contrast variations could cause strain fluctuation in the GPA. Although these may be a concern for quantitative data analysis, applying the same algorithm with the same references areas/mask sizes to compare the strain between both the experimental and simulated images, for all the different defect possibilities, allows qualitative comparison of the nature of different defects.

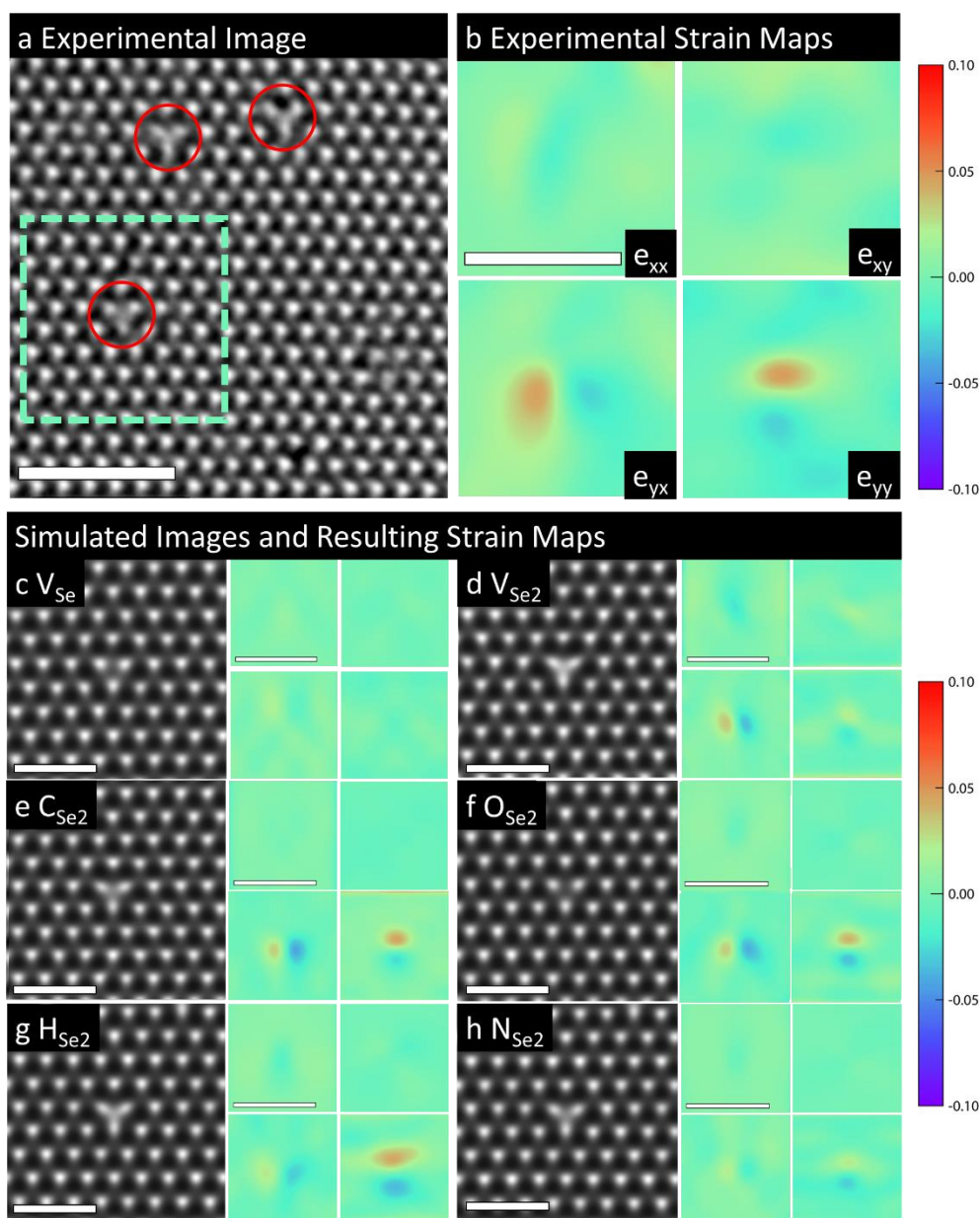


Fig. S8: (a) TEM image of a region containing three divacancy type defects (circled red) and (b) corresponding strain component maps for representative defect within green box in a). In e_{yx} and e_{yy} regions of tension and compression are observed horizontally and vertically across the defect (scale bars: 2nm). GPA strain analysis from TEM image simulations for (c) a Se monovacancy, V_{Se} (d) a Se divacancy, V_{Se_2} (e) a carbon substituted Se divacancy, C_{Se_2} and (f) an oxygen substituted divacancy, O_{Se_2} . (g) a hydrogen substituted divacancy, H_{Se_2} . (h) a nitrogen substituted divacancy, N_{Se_2} . C, N, O simulations match well to the experimental images and strain fields. (Scale bars are 1nm for multislice images and 2nm for GPA maps).

Displacement Cross Section for Se atoms

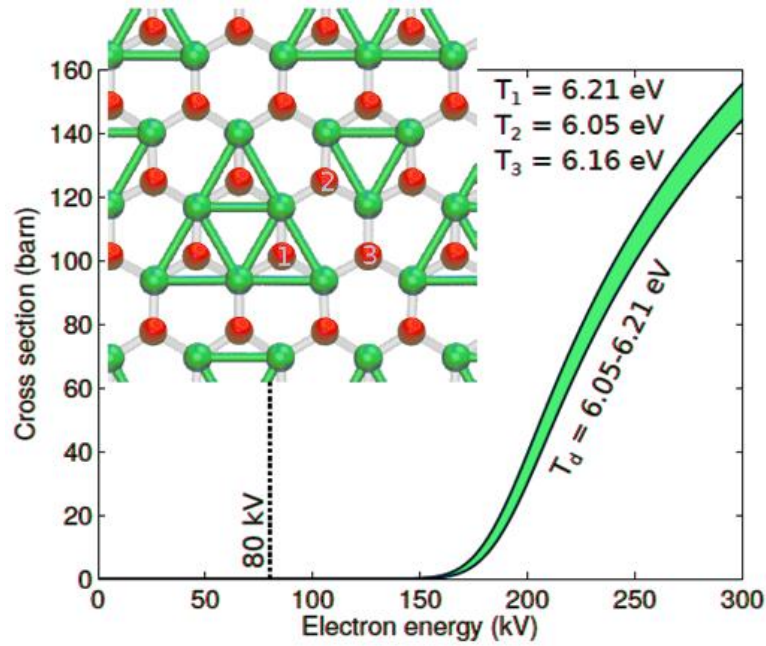


Fig. S9: The cross section for displacing Se atoms calculated using McKinley-Feshbach formalism and 300 K MB velocity distribution for the ions. The thresholds vary between 6.05 and 6.21 eV depending on the position within the CDW structure, as shown in the inset. This range also defines the thickness of the curve.

Defect Density Calculation

The calculation of defect density shown in Fig 4 of the main text was performed by considering the areal density of atoms in pristine monolayer layer material. For a monolayer of NbSe₂, there are 3 atoms per unit cell, and each unit cell has an area of 0.10nm², giving total of 5116 atoms for the entire of 175nm² region. We can then estimate the total % point defect density, defined as the total number of point defects divided by number of total atoms.

To analyse the clustering of defects, the distance, r between the centre of each defect and the centre of its nearest neighbour defect is measured. A histogram is used to distinguish nearest neighbour atom defect clusters ($r < 0.4\text{nm}$) from 2nd nearest neighbour atom defects ($0.4\text{nm} < r < 0.75\text{nm}$). Bins included a 10% error to account for lattice strain and measurement errors. Any defect where the nearest neighbour was further than second nearest neighbours were considered to be isolated ($r > 0.75\text{nm}$).

Equilibrium Defect Density Calculation

From the Boltzmann distribution, an equilibrium concentration of defects in a bulk system can be calculated using:

$$N_v = N e^{\frac{-E_v}{k_B T}}$$

Equation 1: Boltzmann distribution for point defects in solids. N_v : Number of vacancy sites, N : Total number of atomic sites, E_v : Defect formation energy, k_B : Boltzmann's constant, T : Temperature.

Under equilibrium conditions, for the defect formation energies of V_{Se} and V_{Se2} respectively at 293K (1.05eV and 3.53eV), there are 26 V_{Se} defects per metre squared and $6E-42$ V_{Se2} defects per metres squared respectively for $3E19$ atoms per metre squared for monolayer $NbSe_2$ (as computed above). This is vastly different from the experimentally observed number of defects cf. Fig. 4d which are roughly $1E21$ for vacancies.

However, it is not straightforward to apply equilibrium statistics to a hand-made system of 2D materials. In bulk systems, the effects of the environment (*e.g.*, adsorption of reactive species) is limited to the surface and can be neglected. This is clearly not true for 2D materials, which consist of surface only. Besides, even if environmental effects are accounted for (through the proper choice of the chemical potentials when evaluating defect formation energies) a hand-made system, and specifically a $NbSe_2$ -graphene sandwich, is unlikely to be at equilibrium; the system most likely does not have enough time to reach it, and defects created during the fabrication process are likely to have remained in the system (as we show in this work).

DFT analysis to study the nature of point defects

Our density functional theory calculations are carried out within the projector augmented wave framework in the plane-wave basis as implemented in the code VASP.^{61,62} For the defect calculations, we adopted the PBE exchange-correlation functional.⁶³ 400 eV cutoff for the plane-wave basis was found to yield converged total energies. Within PBE, the lattice constant for the unreconstructed primitive cell is 3.49 Å. Spin-orbit coupling leads to splitting of the d-states near the Fermi-level. Since this could affect the gap opening at the Fermi-level and even structural changes, we carried out atomic relaxation with SOC, but this led to no discernible effects in the electronic structure or in the CDW structure. The band structure and DOS with and without SOC are shown in Fig. S6. Fig. S6(c) also shows the resulting CDW structure.

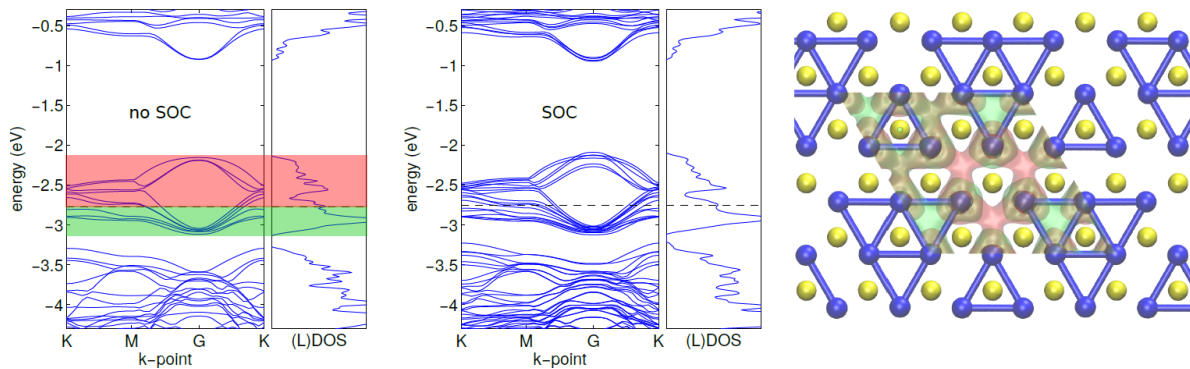


Fig. S10: Band structure and density of states for NbSe₂ in the CDW phase calculated with and without spin-orbit coupling. The atomic structure is also shown and overlaid with partial charge density isosurfaces from the colored regions.

Defects were modeled using 8x8 supercell of monolayer NbSe₂. Spin-polarization has to be accounted for due to the emergence of spin density waves (SDW). Even in such a large supercell, due to the metallic character of the system, 3x3 k-point mesh was required to yield accurate results for the CDW and SDW patterns.

EDX Identification of Nb₂O₅ Oxide Formation

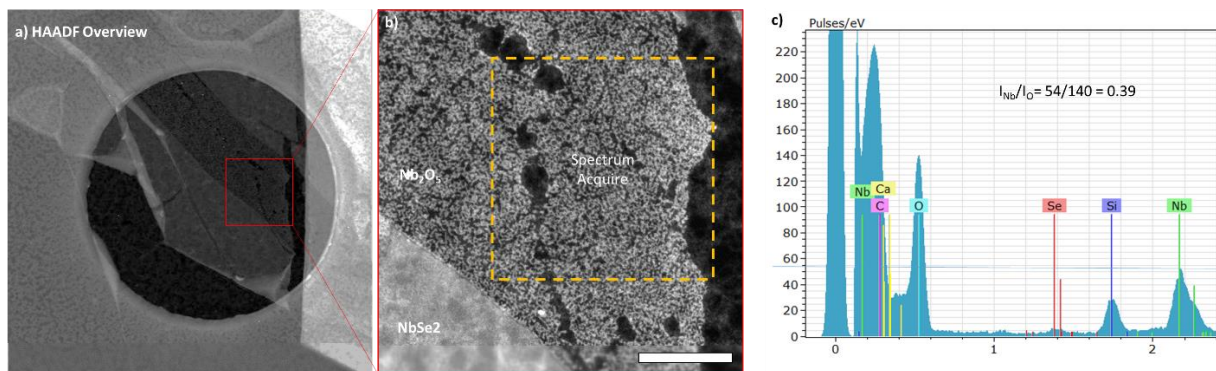


Fig. S11: a,b) HAADF images of graphene encapsulated NbSe₂. c) EDX spectrum from the region shown by the yellow box in (b) with the ratio of intensity of peaks $I_{\text{Nb}}/I_{\text{O}} = 0.39$, which is a close match to the ratio of 0.4 expected for Nb₂O₅.

Alignment of degradation channels with graphene ($10\bar{1}0$) plane

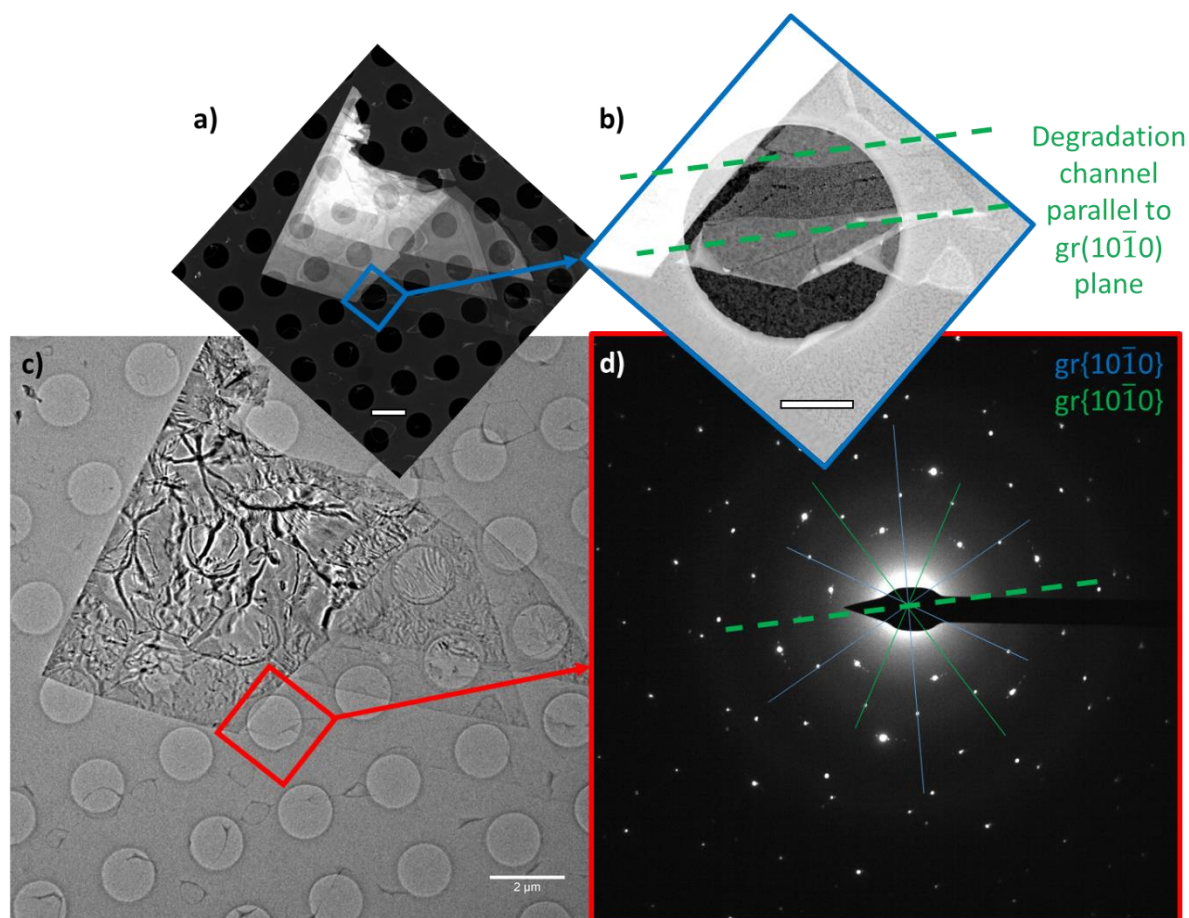


Fig. S12: Diffraction shows degraded strips of NbSe₂ are parallel to a graphene 1010 plane.
a) HAADF overview of region, b) EDX spectrum region from Fig. 6a), c) HRTEM overview of diffraction region d) diffraction pattern taken from square region in c). Planes are drawn orthogonal to corresponding diffraction spots of both graphene sheets to show real space orientation of planes.

DFT analysis of defect magnetic properties

Defect formation energies are defined as:

$$E_f = E_{tot}^{defect} - E_{tot}^{pristine} - \sum_i \mu_i$$

where E_{tot}^{defect} and $E_{tot}^{pristine}$ are the total energy the system with and without the defect, respectively. μ_i is the chemical potential of the added (or removed) atom i . It is important to include the CDW-distortion in the $E_{tot}^{pristine}$ energy, either by directly calculating CDW-distortion in the corresponding supercell or first calculating pristine system using 1H (undistorted) geometry and then adding CDW-stabilization energy to it. This guarantees that the formation energies are independent of the supercell size.

The calculated formation energies and total magnetic moments in the supercell for all considered native defects and impurities are listed in Table S1. The formation energies can be used to determine concentrations of native defects under thermal equilibrium conditions given the chemical potentials that are determined by the growth conditions of the bulk NbSe₂. They can vary between Se-rich conditions (μ_{Se} taken from bulk Se and $\mu_{Nb} = \mu_{NbSe_2}^{bulk} - 2\mu_{Se}^{bulk}$) and the Nb-rich conditions (μ_{Nb} taken from bulk Nb and $\mu_{Se} = 1/2(\mu_{NbSe_2}^{bulk} - \mu_{Nb}^{bulk})$). Energies at both limits are given in Table S1 for native defects. However, in the present case, the growth conditions are unknown and the conditions during electron beam irradiation are certainly out-of-equilibrium, and thus we generally only give the values corresponding to the mid-point between the Se- and Nb-rich limits. In the case of Pt defects, the first value corresponds to Pt bulk and the second to $\mu_{Pt} = \mu_{PtSe_2}^{bulk} - 2\mu_{Se}^{midpoint}$. In the case of C, the first value corresponds to graphene and the second to C₂ dimer. H, N and O defects are only given with respect to the respective dimer molecules.

Table S1: Vacancy formation energies, substitutional energies and magnetic moments for defects in monolayer NbSe₂. As well as substituted and bare (V) vacancy defects adatom Pt, Se and C are also considered (Pt-ad, Se-ad and C-ad respectively). The adatom sites are above a Se lattice site (Se), Nb lattice site (Nb) or a ‘hole-centred’ site in between NbSe₂ hexagons (HC). See methods for further details.

Point Defect	Formation energy (eV)			Magnetization (μ)
	Se-rich conditions	mid-point conditions	Nb-rich conditions	
V_{Nb}	2.23	3.49	4.75	3.65
V_{Se}	1.68	1.05	0.42	0.34
V_{Se2}	4.79	3.53	2.27	0.17
Nb_{Se}	5.34	3.45	1.56	0.16
Pt_{Nb} (Pt metal/PtSe ₂)	0.11 / 0.03			2.65
Pt_{Se} (Pt metal/PtSe ₂)	1.01 / 0.93			8.46
C_{Se} (graphene/C ₂ dimer)	1.69 / -2.78			8.19
C_{Se2} (graphene/C ₂ dimer)	1.78 / -2.69			1.92
H_{Se}	0.88			1.96
H_{Se2}	2.42			3.31
N_{Se}	0.23			0.55
N_{Se2}	-0.52			0.23
O_{Se}	-2.49			10.99
O_{Se2}	-2.68			1.06
Pt-ad(Se) (Pt metal/PtSe ₂)	3.00 / 2.92			
Pt-ad(Nb) (Pt metal/PtSe ₂)	1.67 / 1.59			
Pt-ad(HC) (Pt metal/PtSe ₂)	1.16 / 1.09			
Se-ad(Se)	1.59			
Se-ad(Nb)	1.50			
C-ad(Se) (graphene/C ₂)	5.66 / 1.19			
C-ad(Nb) (graphene/C ₂)	3.09 / -1.38			
C-ad(HC) (graphene/C ₂)	1.70 / -2.77			

Note: Defect notation here is the same and used throughout the text but for reference: V_{Nb}: Nb vacancy; V_{Se}: Se monovacancy; V_{Se2}: Se divacancy; Nb_{Se}: Nb substitution into a Se site; Pt_{Nb}: Pt substitution into a Nb site; Pt_{Se}: Pt substitution into a Se site; C_{Se}: C substitution into a Se site; C_{Se2}: C substitution into a Se divacancy site; H_{Se}: H substitution in a Se site; H_{Se2}: H substitution in a Se divacancy site; N_{Se}: N substitution into a Se site; N_{Se2}: N substitution into a Se divacancy site; O_{Se}: O substitution in a Se site; O_{Se2}: O substitution in a Se divacancy site;

The magnetic moments listed in Table S1 may seem unexpected. These correspond to the total magnetization in the supercell and often arise from spin density wave rather than from localized moments. The SDW can depend sensitively on the supercell size. Moreover, converging the CDW+SDW structure is challenging, likely due to several local energy minima. To probe this, we did the geometry relaxation in two ways: (i) spin-polarized starting from fully random structure, or (ii) first relaxing the system spin-paired and then re-relaxing with spin-polarization. While the resulting energies were usually within few tens of meVs, occasionally the magnetization varied widely. The effect on vacancies was minor. Approach (ii) yielded lower energy for Nb_{Se} and C_{Se2} with magnetizations 0.16 and 1.92, while magnetizations from approach (i) were 7.33 and 4.14, respectively. Approach (i) yielded lower energy for Pt_{Nb}, Pt_{Se}, and C_{Se} with magnetizations 2.65, 8.46, and 8.19, while magnetizations from approach (ii) were 0.09, 0.17, and 1.73, respectively. Thus, it seems that the defects can stabilize SDWs in addition to CDWs, even if the magnetization and spatial distribution of moments may not be accurately described in our relatively small supercell.

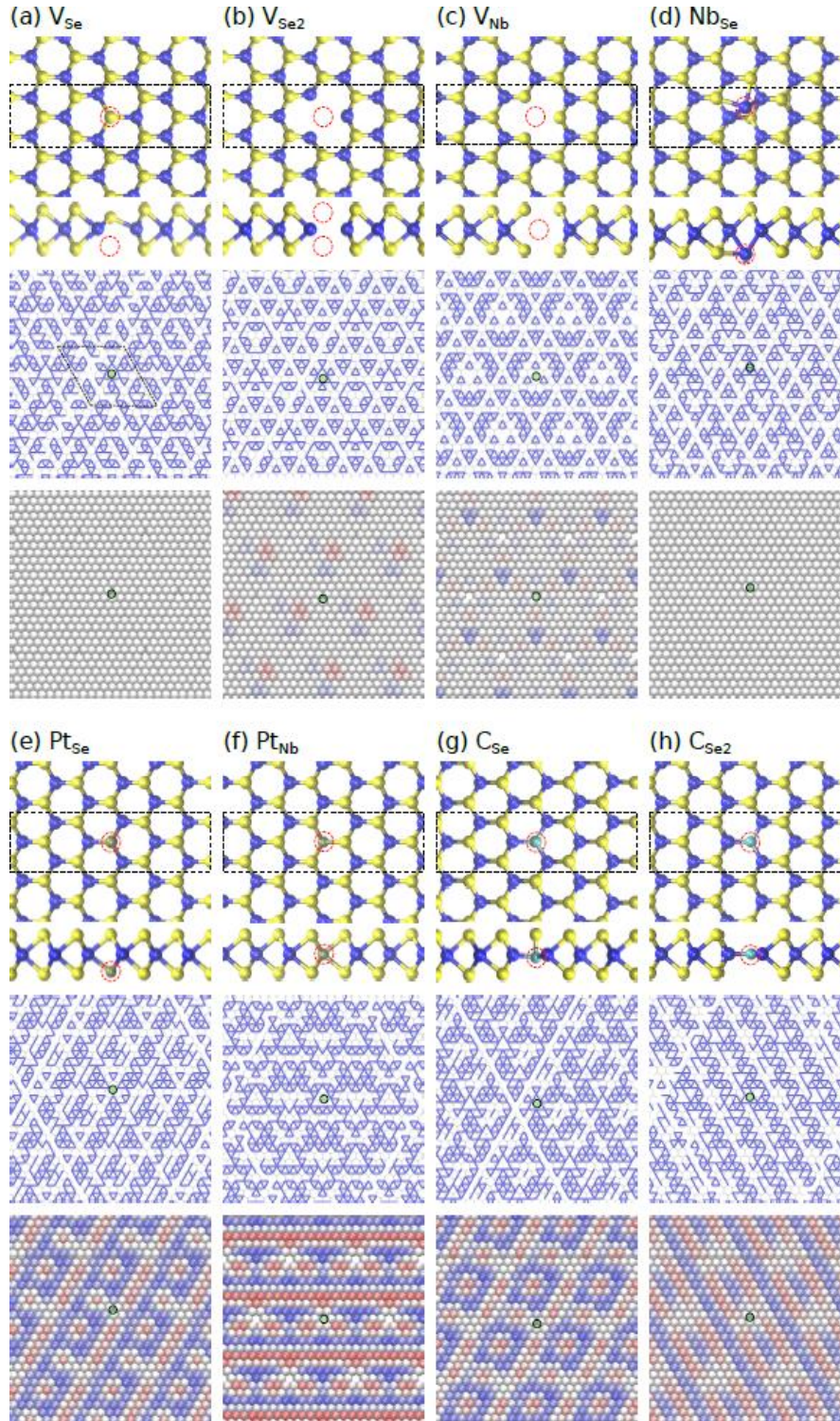


Fig. S13: Atomic structure, CDW, and SDW patterns for V_{Se} , V_{Se2} , V_{Nb} , Nb_{Se} , Pt_{Se} , Pt_{Nb} , C_{Se} , and C_{Se2} defects. In order to visualize the CDW pattern, only Nb-Nb bonds with length less than $3.5 \text{ \AA}$ (essentially matching to the lattice constant) are drawn to highlight contracted and extended bonds. SDW pattern is visualized by showing only the Nb atoms, which are colored by magnetization projected to each atom. The color range is set to go from $-0.5 \mu_B$ (red) to $0.5 \mu_B$ (blue).

The effect of graphene encapsulation on NbSe₂ Electronic Structure

In order to check the level of interaction between NbSe₂ and 1-2 graphene layers, we constructed atomic models for such sandwich structures. The model consists of 5x5 supercell of unstrained NbSe₂, which nearly “lattice matches” with a 7x7 supercell of graphene, resulting in strain of only 0.3% at PBE-D2 level. The geometries of the systems were optimized using semi-empirical vdW corrections added on top of PBE (PBE-D2) and AM05-VV10sol vdW-functional, which has been specifically designed to give good interlayer distances.^{64,65} The PBE-D2 optimized structure is shown in Fig. S7. Layer distance in AM05-VV10sol optimized structure is only slightly larger, varying between 5.11-5.18 Å.

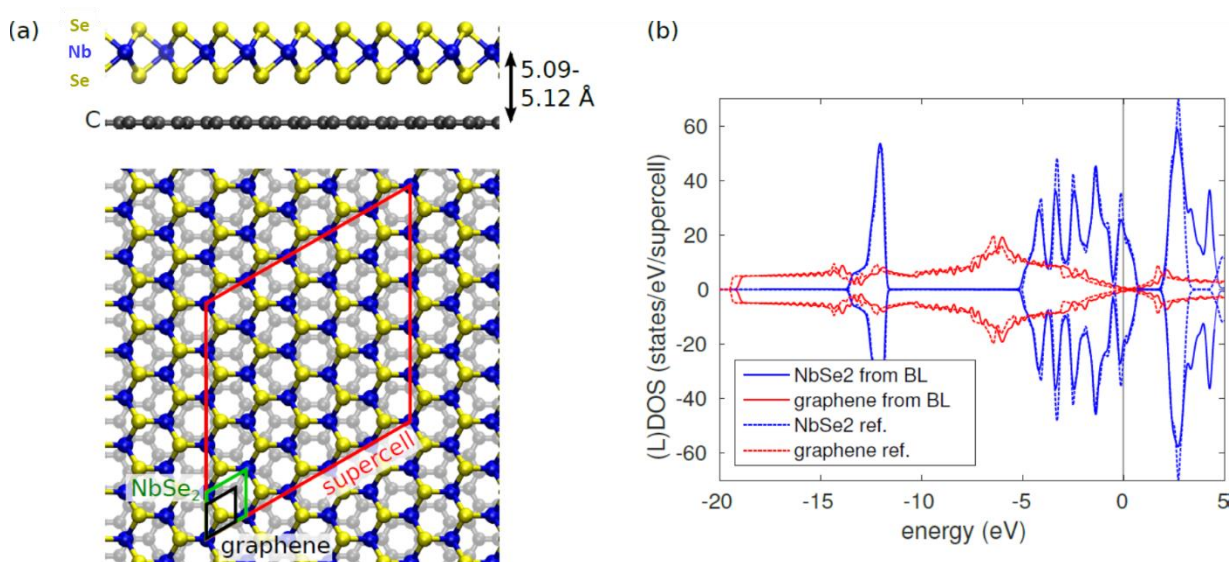


Fig. S14: (a,b) Optimized atomic structure of the NbSe₂/graphene sandwich. The supercell construction is illustrated in (b). (c) Local DOS from the sandwich structure projected to each layer compared to DOS from isolated monolayers

The local density of states from the sandwich structure projected on the NbSe₂ and graphene atoms is shown in Fig. S7(c) and compared to the pristine reference systems. Fermi-level for all three systems is set to 0. The overall shapes of the density of states (DOS) are very similar in the sandwich and reference systems, indicating no major changes in the electronic structure. Since the sandwich consists of two (semi-)metallic materials, some charge transfer is expected, depending on their Fermi-level positions. Fig. S8 shows that Dirac point of graphene in the sandwich structure is located about 0.3 eV above the Fermi-

level, evidencing some degree of charge transfer. On the other hand, it also indicates that the Fermi-levels are fairly close in isolated layers. Moreover, DOS of NbSe₂ in the sandwich and reference systems overlap energetically very well. That is, the large DOS of NbSe₂ at the Fermi-level leads to essentially no shift upon charging.

We calculated Bader charges from the sandwich and reference systems. Within the supercell, 0.56 e is transferred from graphene to the NbSe₂ layer, corresponding to -0.011 e per graphene and 0.022 e per NbSe₂ primitive cell. In addition, there is further charge redistribution within the NbSe₂ sheet, where Nb atoms have in fact lost 0.010 e per atom, while there is a gain of 0.032 e per the two Se atoms.

In essence, since the sandwich structure consists of two metallic systems with nearly aligned Fermi-levels, properties of defects located within NbSe₂ should not be affected by the graphene sheet. Therefore we use the monolayer NbSe₂ as this allows us freely vary the supercell size and also offers quite significant speedup in the calculations. The situation will be obviously different for adatoms (or interstitial atoms), but are not considered in this work.