Supplementary Information

Tunability in the optical response of defective monolayer WSe$_2$ by computational analysis

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Formation Energies

Defect formation energies \( E_f \) were calculated at the DFT/PBE level using the expression

\[
E_f = \left[ E_{\text{defect}} + n_i \mu_i \right] - E_{\text{pristine}},
\]

where \( E_{\text{defect}} \) is the total energy of the WSe\(_2\) supercell with defects; \( E_{\text{pristine}} \) is the total energy of the pristine WSe\(_2\) supercell; \( n_i \) is the number of \( i \) elements (W or Se) removed from pristine WSe\(_2\) to create the defects; and \( \mu_i \) is the chemical potential of element \( i \). For the SV, DV, WV, T\(_1\), T\(_2\), T\(_3\) defects in 2D WSe\(_2\), \( n_i \mu_i = \mu_{\text{Sc}}, 2\mu_{\text{Sc}}, \mu_{\text{W}}, 6\mu_{\text{Sc}}, 10\mu_{\text{Sc}}, 14\mu_{\text{Se}} \), respectively. The chemical potential was calculated by \( \mu_{W} + 2\mu_{\text{Se}} = \mu_{\text{WSe}} \), \(^1\) where \( \mu_{W}, \mu_{\text{Sc}}, \) and \( \mu_{\text{WSe}} \) are the chemical potentials for W, Se, and WSe\(_2\), respectively. \( \mu_{\text{WSe}} \) was calculated as the total energy per primitive cell of pristine WSe\(_2\), \( \mu_{W}^{\text{Max}} \) is the total energy per atom of a bcc W metal, and \( \mu_{\text{Se}}^{\text{Max}} \) the total energy per atom of a grey Se crystal.

At the DFT/PBE level we obtained \( \mu_{\text{WSe}} = -21.67 \) eV, \( \mu_{W}^{\text{Max}} = -13.02 \) eV, \( \mu_{\text{Se}}^{\text{Max}} = -3.50 \) eV; \( \mu_{W}^{\text{Min}} = \mu_{\text{WSe}} - 2\mu_{\text{Se}} = -14.68 \) eV, and \( \mu_{\text{Se}}^{\text{Min}} = \left( \mu_{\text{WSe}} - \mu_{W}^{\text{Max}} \right)/2 = -4.33 \) eV. For a W rich environment, \( \mu_{W} = \mu_{W}^{\text{Max}} \) and \( \mu_{\text{Se}} = \mu_{\text{Se}}^{\text{Min}} \), and the defect formation energies of 1.85 eV, 3.23 eV, 5.17 eV, 6.91 eV, 11.20 eV, and 15.38 eV, for SV, DV, WV, T\(_1\), T\(_2\), and T\(_3\), respectively, were calculated, while for an Se rich environment, where \( \mu_{\text{Se}} = \mu_{\text{Se}}^{\text{Max}} \) and \( \mu_{W} = \mu_{W}^{\text{Min}} \), defect formation energies were 2.68 eV, 4.89 eV, 3.51 eV, 11.88 eV, 19.49 eV, and 26.98 eV, for SV, DV, WV, T\(_1\), T\(_2\), and T\(_3\) defects, respectively. The results for SV, DV, and WV agree with previous DFT calculations.\(^1\)

Reference

**Table S1.** RPA excitation energies for monolayer WSe$_2$ with T$_1$, T$_2$, and T$_3$ defects: D$_1$, D$_2$, D$_3$, and D$_4$ bound excitons (in eV).

<table>
<thead>
<tr>
<th></th>
<th>D$_1$</th>
<th>D$_2$</th>
<th>D$_3$</th>
<th>D$_4$</th>
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<tr>
<td>T$_1$</td>
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<tr>
<td>T$_2$</td>
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<td>0.11</td>
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<td>T$_3$</td>
<td>1.26</td>
<td>1.12</td>
<td>0.83</td>
<td>0.10</td>
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</table>
Figure S1. PBE+SOC band structures for monolayer WSe$_2$ with a SV defect using (a) 2×2×1, (b) 3×3×1, (c) 4×4×1, and (d) 5×5×1 supercells. Defect bands are numerically labelled.
Figure S2. Convergence of the absorption spectrum of monolayer WSe$_2$ with a SV defect with respect to $k$-point sampling. Black, red, and green are for $3 \times 3 \times 1$, $4 \times 4 \times 1$, and $5 \times 5 \times 1$ $k$ samplings, respectively.
Figure S3. PBE+SOC band structures for monolayer WSe$_2$ with (a) SV, (b) DV, (c) WV, (d) T$_1$, (e) T$_2$, and (f) T$_3$ defects. Bound defect bands are numerically labelled.
Figure S4. Phonons in pristine 2D WSe$_2$: (a) phonon dispersion, and (b) phonon eigenvectors for 1$^{st}$ order Raman active modes E$'$ and A$_1$'.

(a)

(b)

\[ E'(1)  \quad E'(2)  \quad A_1' \]