Atomic-scale mechanisms of defect- and light-induced oxidation and degradation of InSe

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S1. Details of energetics and charge transfer for gas adsorption

Table S1. Adsorption energy ($E_a$) for physisorption of H$_2$O and O$_2$ molecules and the charge transfer ($\Delta q$) from these molecules to perfect and defective InSe sheets. Note that a positive $\Delta q$ indicates the transfer of electrons from the molecules to the surface.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Adsorbate</th>
<th>$E_a$ (eV)</th>
<th>$\Delta q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect InSe</td>
<td>H$_2$O</td>
<td>-0.17</td>
<td>-0.020</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>-0.12</td>
<td>-0.023</td>
</tr>
<tr>
<td>MV-contained InSe</td>
<td>H$_2$O</td>
<td>-0.41</td>
<td>-0.090</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>-0.10</td>
<td>-0.027</td>
</tr>
<tr>
<td>Preoxidized perfect InSe</td>
<td>H$_2$O</td>
<td>-0.33</td>
<td>-</td>
</tr>
<tr>
<td>Preoxidized MV-contained InSe</td>
<td>H$_2$O</td>
<td>-0.34</td>
<td>-</td>
</tr>
</tbody>
</table>

S2. Intrinsic and thickness dependent electronic properties of InSe

Figure S1. Thickness-dependent band structures of InSe (from 1L to 4L) calculated by GGA method.
S3. Adsorption and motion of $\text{O}_2$ and $\text{H}_2\text{O}$ above InSe

**Figure S2.** Adsorption of $\text{O}_2$ (a, left panel) and $\text{H}_2\text{O}$ (b, left panel) on perfect InSe. LDOS for $\text{O}_2$ (a, right panel) and $\text{H}_2\text{O}$ molecule (b, right panel) adsorbed on perfect InSe with the Fermi level (dashed line) aligned at zero. States of $\text{O}_2/\text{H}_2\text{O}$ (total system) are plotted by the red (black) lines. (c) LDOS for $\text{O}_2$ molecule chemisorbed at the $\text{V}_{\text{Se}}$ site of InSe. (d) Isosurface plots of the differential charge density after $\text{O}_2/\text{H}_2\text{O}$ physisorption on perfect InSe, where the green/blue color denotes depletion/accumulation of electrons (left panel).
Figure S3. Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of (a) $\text{O}_2$ and (b) $\text{O}_2^-$ on perfect InSe sheet. In, Se, and O atoms are colored in purple, yellow, and red, respectively.
Figure S4. (a) Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of $\text{O}_2^-$. (b) Chemical dissociation of $\text{O}_2^-$ molecule on MV-V$_\text{Se}$ contained InSe. Energetic profiles of the reaction pathway calculated by CI-NEB calculations. The IS, TS and FS represent the initial, transition, and final states, respectively. In, Se, and O atoms are colored in purple, yellow, and red, respectively. The position of the V$_\text{Se}$ is represented by the circle.
**Figure S5.** Snapshot of the motion of water molecule on perfect InSe calculated by AIMD at 300 K. Atoms O, H, In, and Se are colored in red, white, purple, and yellow, respectively.
Figure S6. Snapshots of AIMD simulations of H$_2$O on pre-oxidized (a) perfect and (b) mono-vacancy contained InSe at 300 K. Atoms O, H, In, and Se are colored in red, white, purple, and yellow, respectively.
Figure S7. (a) Chemical dissociation of H$_2$O molecule on MV-VSe-contained InSe. Upper panel: Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of H$_2$O. Lower panel: Energetic profiles of the reaction pathway calculated by CI-NEB calculations. The IS, TS and FS represent the initial, transition, and final states, respectively. In, Se, H and O atoms are colored in purple, yellow, white and red, respectively. Atomic configuration and LDOS for (b) O and (c) OH defects on the perfect InSe surface with the Fermi level (dashed line) aligned at zero. States of O/OH (the total system) are denoted by the red (black) lines.

In addition, we have also calculated the energy barrier ($E_b$) for H$_2$O molecule splitting near the Se vacancy (see Figure S7a). It is seen that different from O$_2$ molecule which can easily dissociate at the V$_{Se}$ site, H$_2$O has a large $E_b$ of $\sim$2.9 eV, suggesting that H$_2$O cannot dissociate at the vacancy site at a moderate temperature. Interestingly, after H$_2$O dissociation, the formed OH defect leads to a shift of nearest Se atom out of the surface (see the upper panel of Figure S7a).

To examine the effect of the O/OH defect on the electronic properties of InSe, we have studied the local density of states (LDOS) of the InSe-O and InSe-OH systems, and the results are presented in Figures S7b and c. Upon being adsorbed on InSe surface, the O is situated right above the Se atom (see the left panel of Figure S7b) and the OH adopts a tilted configuration with the O-H bond pointing away from the surface (see the right panel of Figure S7c). The lowest unoccupied molecular orbital (LUMO) state ($2\pi^*$) and the highest occupied molecular orbital (HOMO) state ($2\pi$) of
the O are below the Fermi level, suggesting that electrons can be effectively trapped by the O defect. For the OH defect, the highest occupied molecular orbital \(1b_1\) (HOMO) is below the empty “E” defect level. Our differential charge density (DCD) \(\Delta \rho(r)\) analysis shows that the O and OH are molecular acceptors for perfect InSe with the charge transfer of 0.27 and 0.17 e from the surface to O and OH, respectively, amounting to \(1.16 \times 10^{12}\) and \(0.73 \times 10^{12}\) el/cm\(^2\) according to our current atomic model with O and OH coverage of 6.25% (see Figure S8).

**Figure S8.** The plane-averaged DCD \(\Delta \rho(z)\) (red line) and the amount of transferred charge \(\Delta Q(z)\) (green line) for (a) O and (b) OH defects on the perfect InSe surface.