Supporting Information

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_2O and O_2 molecules and the charge transfer (Δq) from these molecules to perfect and defective InSe sheets. Note that a positive Δq indicates the transfer of electrons from the molecules to the surface.

Structure	Adsorbate	E_a (eV)	Δq *(e)*
Perfect InSe	H_2O	-0.17	-0.020
	O_2	-0.12	-0.023
MV-contained InSe	H_2O	-0.41	-0.090
	O_2	-0.10	-0.027
Preoxidized perfect InSe	H_2O	-0.33	-
Preoxidized MV-contained InSe	H_2O	-0.34	-

S2. Intrinsic and thickness dependent electronic properties of InSe

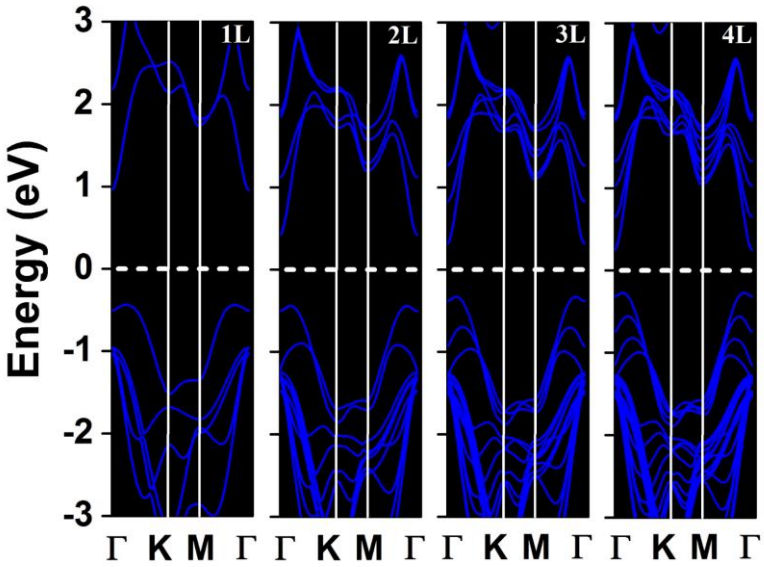

Figure S1. Thickness-dependent band structures of InSe (from 1L to 4L) calculated by GGA method.

S3. Adsorption and motion of O_2 and H_2O above InSe

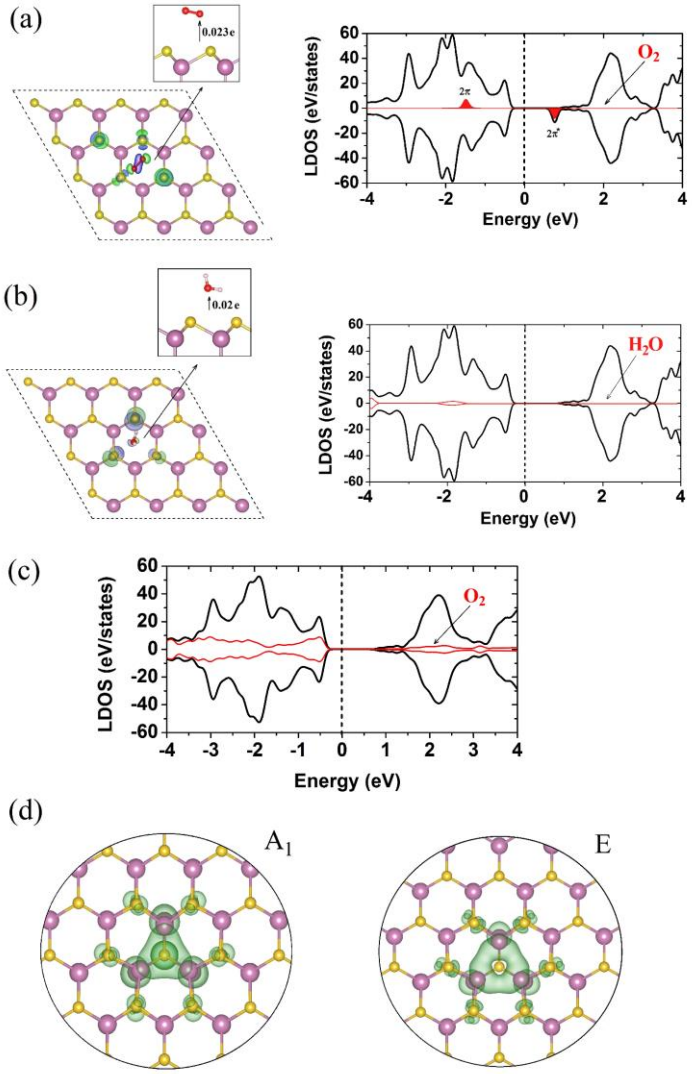

Figure S2. Adsorption of O_2 (a, left panel) and H_2O (b, left panel) on perfect InSe. LDOS for O_2 (a, right panel) and H_2O molecule (b, right panel) adsorbed on perfect InSe with the Fermi level (dashed line) aligned at zero. States of O_2/H_2O (total system) are plotted by the red (black) lines. (c) LDOS for O_2 molecule chemisorbed at the V_{Se} site of InSe. (d) Isosurface plots of the differential charge density after O_2/H_2O physisorption on perfect InSe, where the green/blue color denotes depletion/accumulation of electrons (left panel).

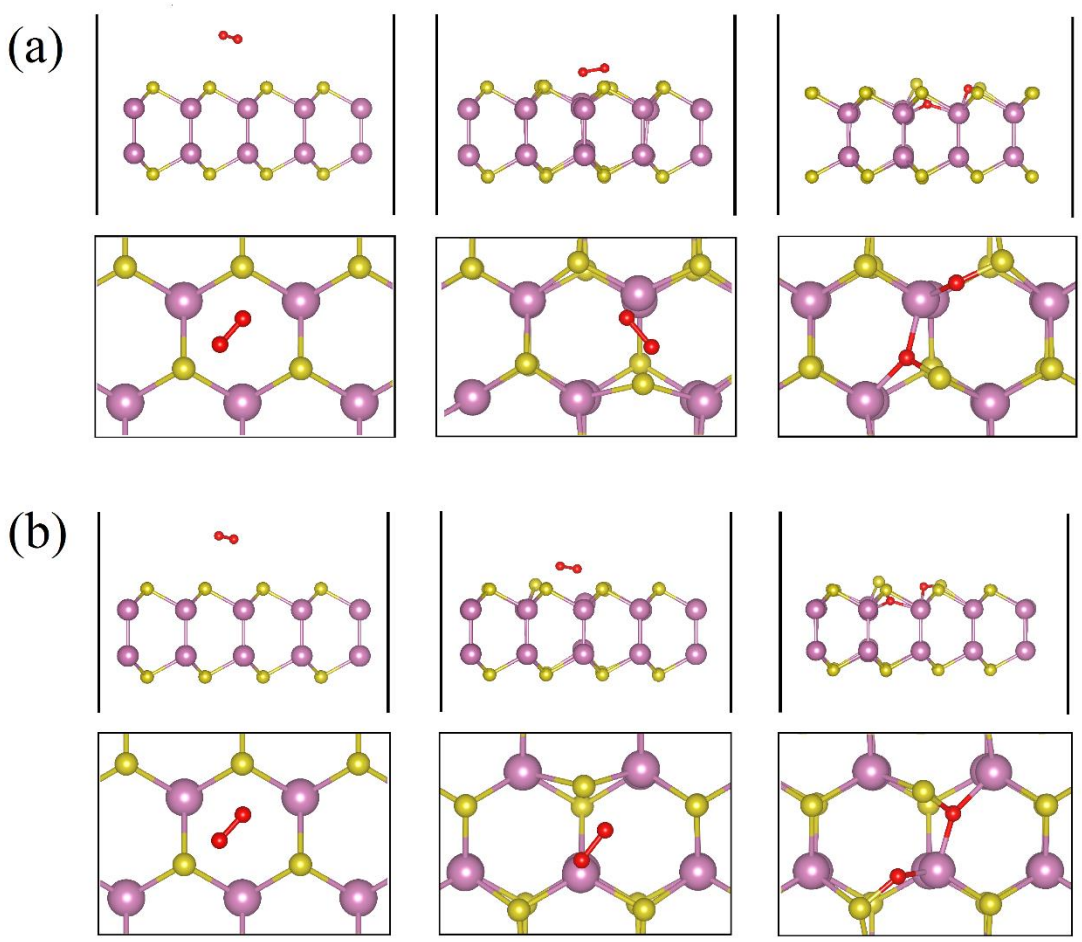

Figure S3. Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of (a) O_2 and (b) O_2^- on perfect InSe sheet. In, Se, and O atoms are colored in purple, yellow, and red, respectively.

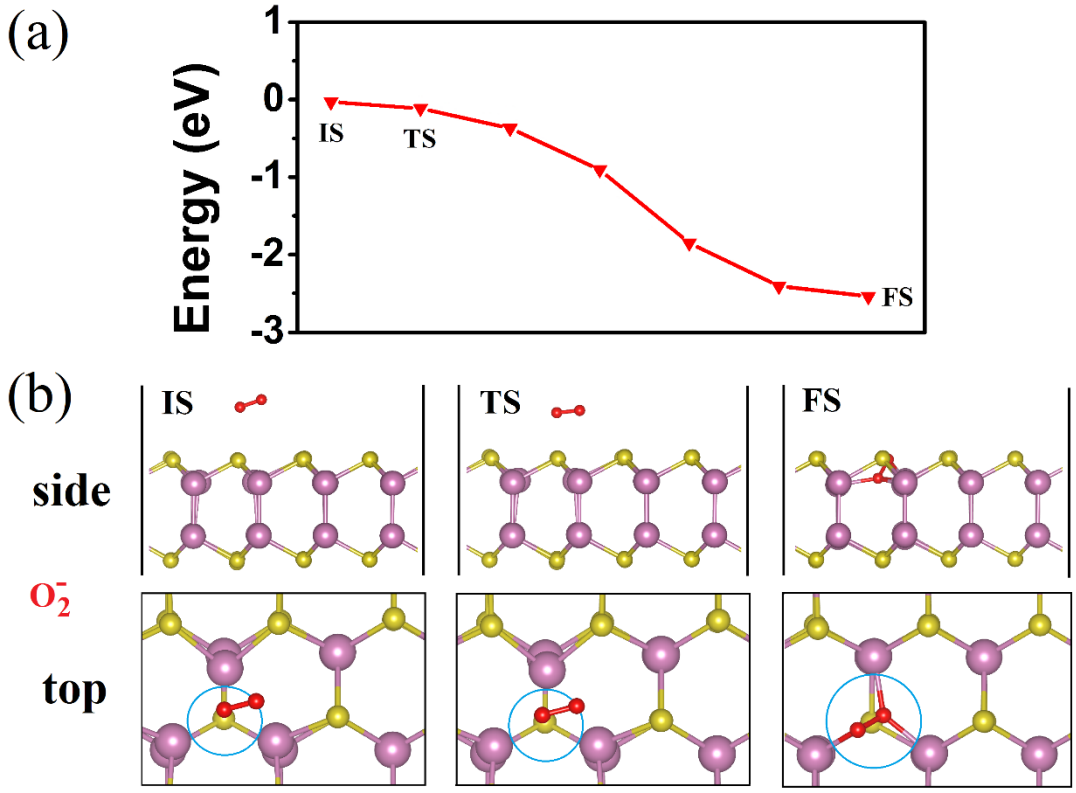

Figure S4. (a) Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of O_2^-. (b) Chemical dissociation of O_2^- molecule on MV-V_{Se} contained InSe. Energetic profiles of the reaction pathway calculated by CI-NEB calculations. The IS, TS and FS represent the initial, transition, and final states, respectively. In, Se, and O atoms are colored in purple, yellow, and red, respectively. The position of the V_{Se} is represented by the circle.

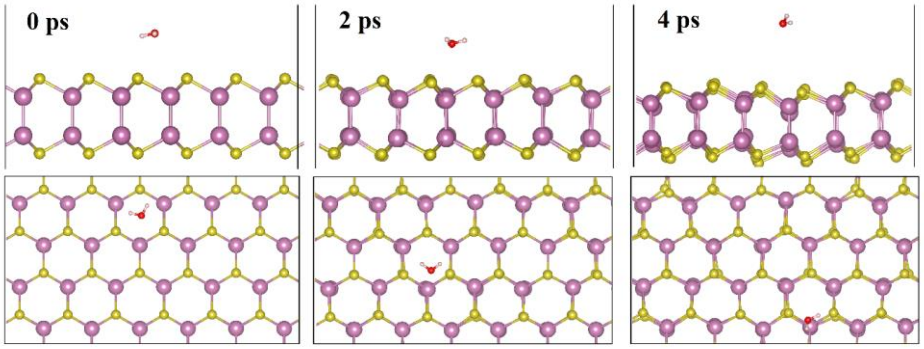

Figure S5. Snapshot of the motion of water molecule on perfect InSe calculated by AIMD at 300 K. Atoms O, H, In, and Se are colored in red, white, purple, and yellow, respectively.

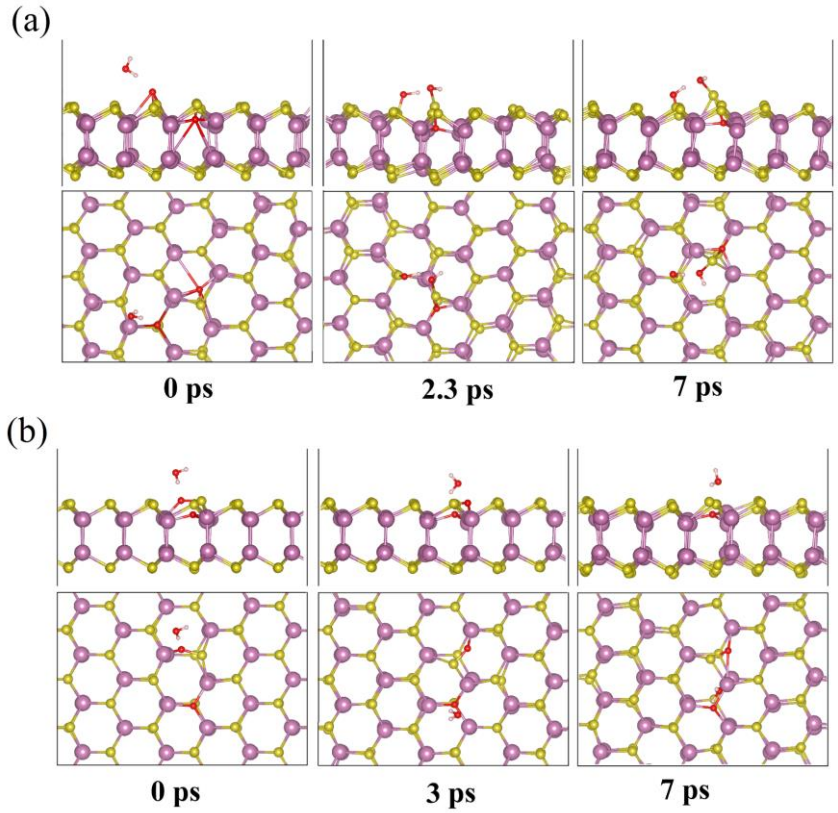

Figure S6. Snapshots of AIMD simulations of H_2O on pre-oxidized (a) perfect and (b) mono-vacancy contained InSe at 300 K. Atoms O, H, In, and Se are colored in red, white, purple, and yellow, respectively.

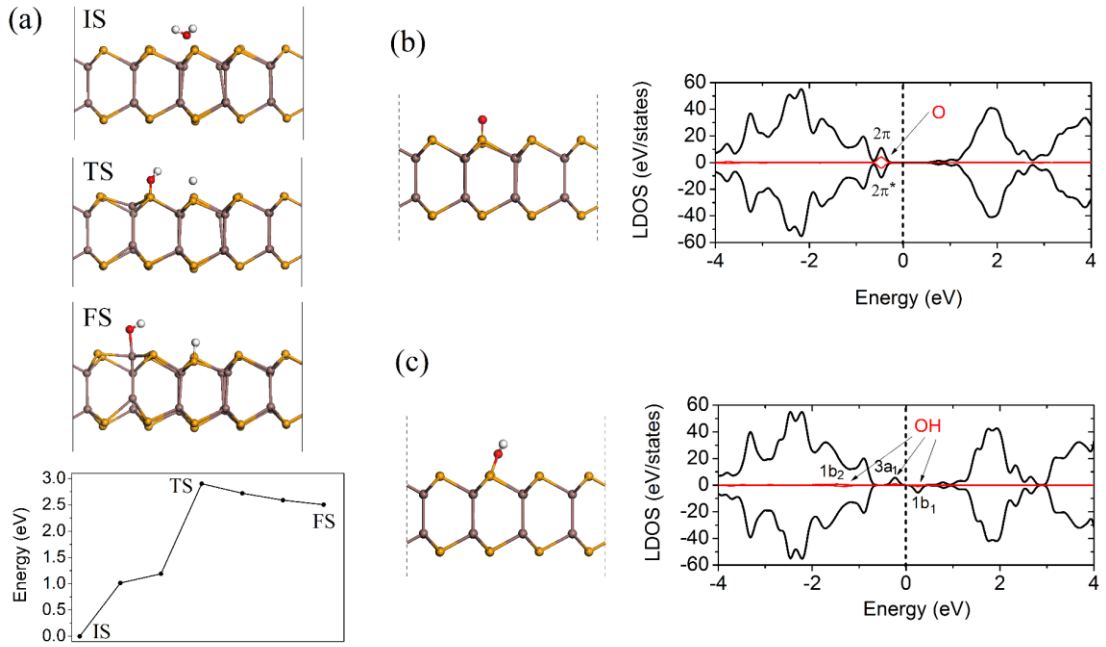

Figure S7. (a) Chemical dissociation of H_2O molecule on MV-VSe-contained InSe. Upper panel: Atomic configurations from the physisorbed to the chemisorbed state in the dissociation process of H_2O. Lower panel: Energetic profiles of the reaction pathway calculated by CI-NEB calculations. The IS, TS and 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_2O 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_2O has a large E_b of ~2.9 eV, suggesting that H_2O cannot dissociate at the vacancy site at a moderate temperature. Interestingly, after H_2O 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 titled 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 (2π) 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 1.16×10^{12} and 0.73×10^{12} e/cm^2 according to our current atomic model with O and OH coverage of 6.25% (see Figure S8).

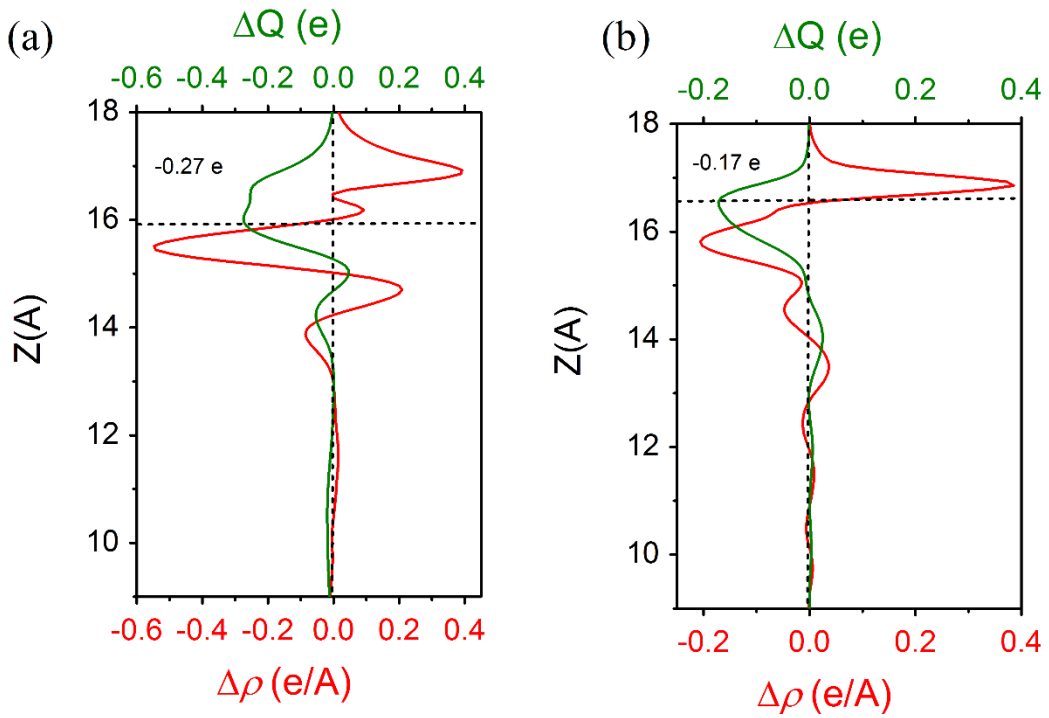

Figure S8. The plane-averaged DCD $\Delta\rho(z)$ (red line) and the amount of transferred charge $\Delta Q(z)$ (green line) for (a) O and (b) OH defects on the perfect InSe surface.