Supporting information for

Unveiling Chemical Reactivity and Oxidation of 1T Phased Group VI Disulfide

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Table of Contents

1. Band structures of MS$_2$ ................................................................. 3
2. Computational models ...................................................................... 4
3. Pristine surface ............................................................................... 5
   3.1 H$_2$O adsorption on pristine surfaces of MS$_2$ ............................ 5
   3.2 O$_2$ adsorption on pristine surfaces of MS$_2$ ............................ 6
4. Sulfur vacancy ............................................................................... 7
   4.1 H$_2$O adsorption on sulfur vacancy sites of MS$_2$ ....................... 7
   4.2 O$_2$ adsorption on sulfur vacancy sites of MS$_2$ ....................... 8
5. O-doped surface ........................................................................... 10
   5.1 O$_2$ and H$_2$O adsorption on O-doped HfS$_2$ and ZrS$_2$ surfaces .... 10
   5.2 O-doped TiS$_2$ surface ............................................................... 12
6. Edges .......................................................................................... 13
   6.1 H$_2$O adsorption on edge M sites of MS$_2$ ................................. 13
   6.2 O$_2$ adsorption on edge M sites of MS$_2$ ................................. 14
   6.3 Formation of TiO$_x$ ................................................................. 15
7. Appendix ....................................................................................... 16
1. Band structures of MS$_2$

Figure S1. Band structure of TiS$_2$ at GGA-PBE level.

Figure S2. Band structure of ZrS$_2$ at GGA-PBE level.
2. Computational models

Figure S3. Computational models of HfS$_2$ (same models are used for TiS$_2$ and ZrS$_2$) for the surface and edge (with 50% S coverage) calculations with cell size of 4*4.
3. Pristine surface

3.1 $\text{H}_2\text{O}$ adsorption on pristine surfaces of $\text{MS}_2$

Figure S4. Adsorption structures and energies of $\text{H}_2\text{O}$ on pristine MS$_2$ (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.
3.2 O$_2$ adsorption on pristine surfaces of MS$_2$

![Figure S5. Adsorption structures and energies of O$_2$ on pristine MS$_2$ (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.](image)

![Figure S6. Direct surface oxidation on pristine TiS$_2$ (001) surface, Ti, S and O are marked in grey, yellow and red respectively.](image)
4. Sulfur vacancy

4.1 H$_2$O adsorption on sulfur vacancy sites of MS$_2$

Figure S7. Adsorption structures and energies of H$_2$O on a sulfur vacancy site of MS$_2$ (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.

Figure S8. Proposed reaction pathway of water oxidation process at a TiS$_2$ surface vacancy site, the numbers in blue are calculated kinetic barriers for SH formation and H2S formation.
Figure S9. Proposed reaction pathway of water oxidation process at a ZrS$_2$ surface vacancy site. The number in blue is calculated kinetic barrier for SH formation. The formation of H$_2$S is energy unfavorable by 0.79 eV. The structures are very similar with the case of HfS$_2$ as shown in Figure 2b.

### 4.2 O$_2$ adsorption on sulfur vacancy sites of MS$_2$

Figure S10. Adsorption structures and energies of O$_2$ on a sulfur vacancy site of MS$_2$ (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2. Charge transfer from O$_2$ to MS$_2$ is analyzed by Bader charge analysis.
Figure S11. Structure evolution of O$_2$ adsorbed at a sulfur vacancy site. The structures shown in the Figure are examples from HfS$_2$, but can be applied to TiS$_2$ and ZrS$_2$ as well.

Figure S12. The shrink of lattice site into the inner part of the MS$_2$ comparing with initial S site (shadowed yellow) by O substitution, and O$_2$ and H$_2$O may attack these surrounding metals.
5. O-doped surface

5.1 $\text{O}_2$ and $\text{H}_2\text{O}$ adsorption on O-doped HfS$_2$ and ZrS$_2$ surfaces

Figure S13. Side and top views of $\text{H}_2\text{O}$ (left side) and $\text{O}_2$ (right side) adsorption on an O-doped HfS$_2$ surface.

Figure S14. Side and top views of $\text{H}_2\text{O}$ (left side) and $\text{O}_2$ (right side) adsorption on an O-doped ZrS$_2$ surface.
Figure S15. Proposed reaction pathway of O$_2$ induced oxidation on an O doped HfS$_2$ surface.
Figure S16. Proposed reaction pathway of H\textsubscript{2}O induced oxidation on an O doped HfS\textsubscript{2} surface.

Figure S17. Geometry optimization of an S\textsubscript{2} dimer on the O doped HfS\textsubscript{2} surface.

5.2 O-doped TiS\textsubscript{2} surface

Figure S18. Geometry optimization of H\textsubscript{2}O adsorption on an O doped TiS\textsubscript{2} surface and similar results can be found for non-polar O\textsubscript{2} adsorption.
6. Edges

6.1 H$_2$O adsorption on edge M sites of MS$_2$

Figure 20. Proposed reaction pathways of H$_2$O induced oxidation at TiS$_2$ edge sites with 50% S coverage. The numbers denote for energy barriers of each step. All the energies and kinetic barriers are obtained from ref. 16 [J. Phys. Chem. C 2015, 119, 15707].
Figure 21. Proposed reaction pathways of H$_2$O induced oxidation at ZrS$_2$ edge sites with 50% S coverage. The numbers denote for energy barriers of each step.

6.2 O$_2$ adsorption on edge M sites of MS$_2$

Figure 22. Proposed reaction pathways of O$_2$ induced oxidation at TiS$_2$ edge sites with 50% S coverage. The numbers denote for energy barriers of each step.
Figure 23. Proposed reaction pathways of O$_2$ induced oxidation at ZrS$_2$ edge sites with 50% S coverage. The numbers denote for energy barriers of each step.

6.3 Formation of TiO$_x$

Figure 24. The adsorption of O$_2$ and H$_2$O at oxidized TiS$_2$ edge, the x ranges from 0-2, denotes as TiS$_3$, TiS$_2$O$_1$ and TiS$_1$O$_2$ respectively. The oxidized area is in shadow and TiO$_3$ can be seen in Figure 4 from the main text.
7. Appendix

Figure 25. $\text{O}_2$ adsorption on TiS$_2$ S edge sites with 50% S coverage.

Figure 26. $\text{O}_2$ adsorption on an O-doped HfS$_2$ surface.

Table S1. Bond length of M-S in pristine MS$_2$, and M-O in O doped MS$_2$.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>M-S</th>
<th>M-O</th>
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<tbody>
<tr>
<td>Hf</td>
<td>2.55</td>
<td>2.10</td>
</tr>
<tr>
<td>Zr</td>
<td>2.57</td>
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<tr>
<td>Ti</td>
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Table S2. Adsorption energies of O$_2$ and H$_2$O on various sites of MS$_2$, units are in eV. Adsorption structures can be seen in each part of the supporting information.

<table>
<thead>
<tr>
<th></th>
<th>MS$_2$</th>
<th>O$_2$</th>
<th>H$_2$O</th>
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</thead>
<tbody>
<tr>
<td>Pristine surface</td>
<td>TiS$_2$</td>
<td>-0.07</td>
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<tr>
<td></td>
<td>ZrS$_2$</td>
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</tr>
<tr>
<td></td>
<td>HfS$_2$</td>
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<tr>
<td>Sulfur vacancy</td>
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<tr>
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<td>ZrS$_2$</td>
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<tr>
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<td>O-doped surface</td>
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