Supporting information for

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

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[†]These authors contributed equally to this work.

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1. Band structures of MS_2

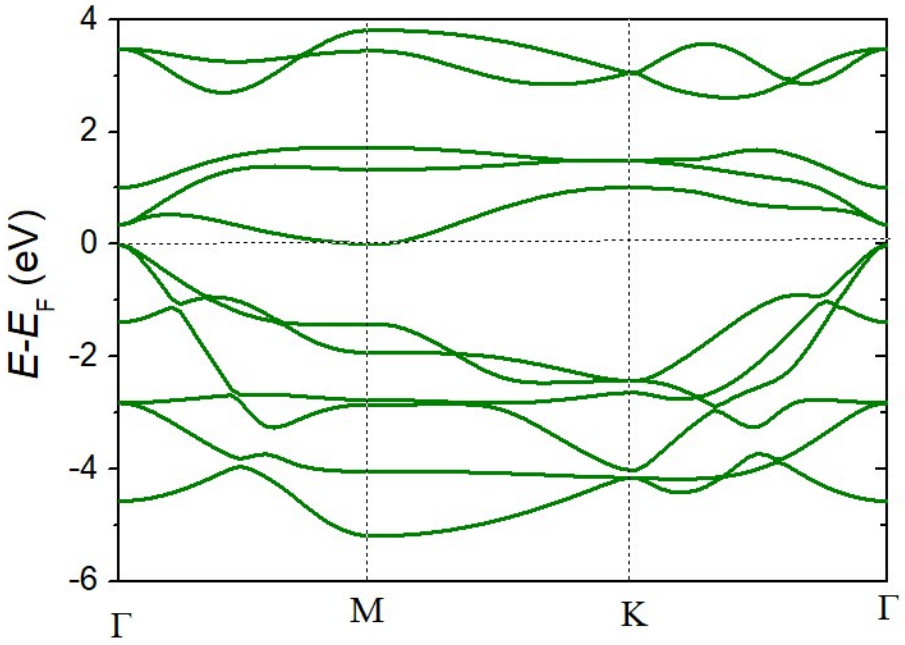

Figure S1. Band structure of TiS_2 at GGA-PBE level.

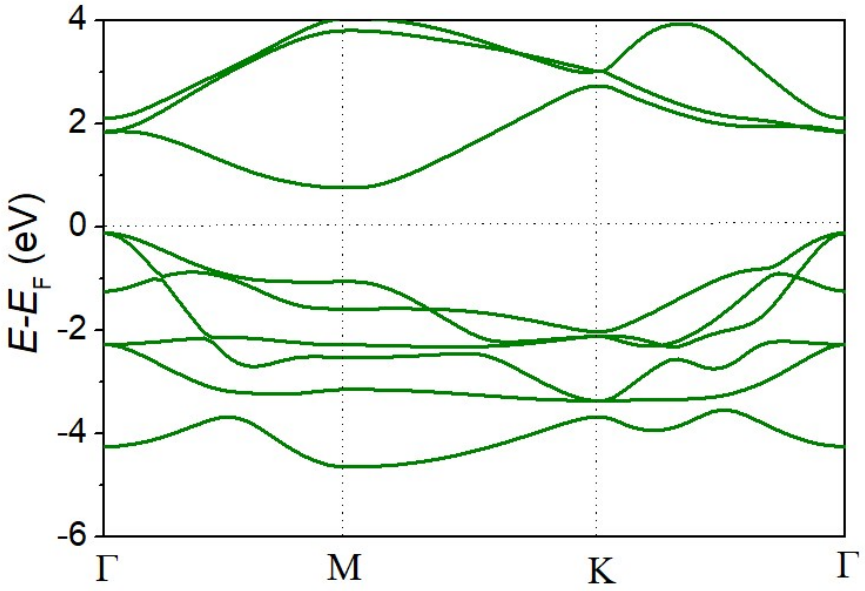

Figure S2. Band structure of ZrS_2 at GGA-PBE level.

2. Computational models

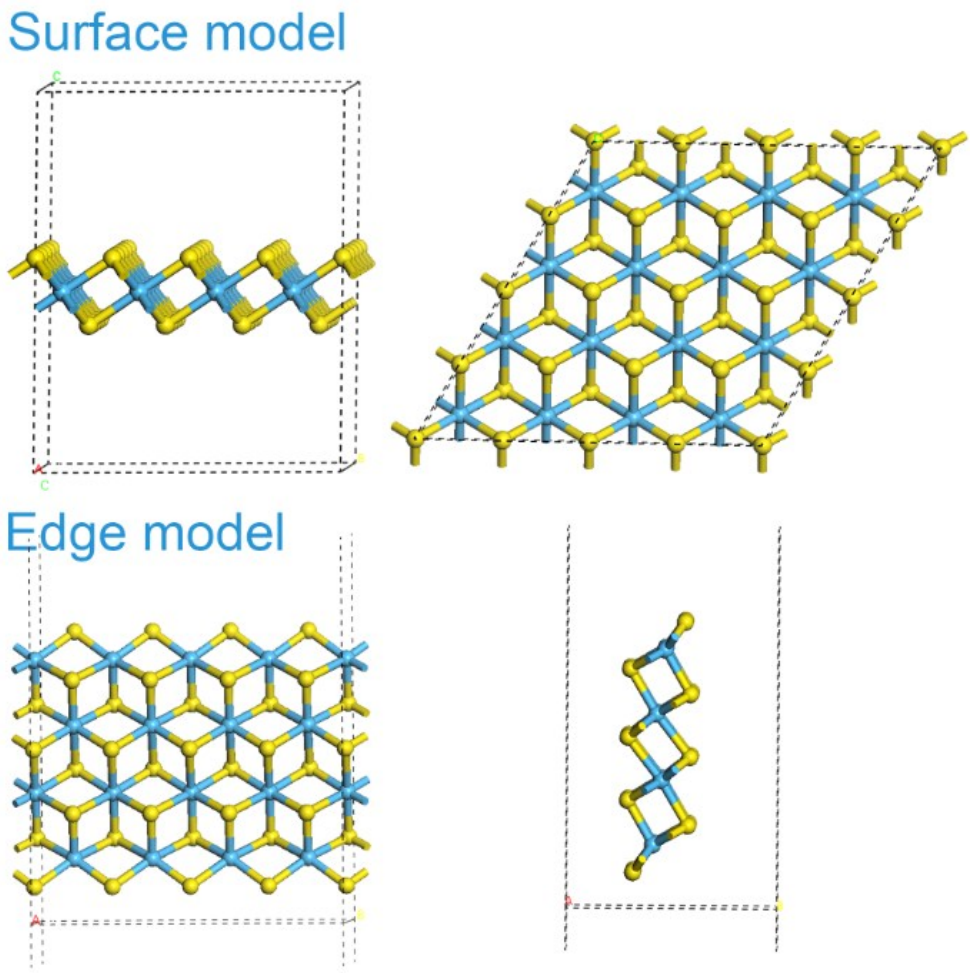

Figure S3. Computational models of HfS_2 (same models are used for TiS_2 and ZrS_2) for the surface and edge (with 50% S coverage) calculations with cell size of 4*4.

3. Pristine surface

3.1 H_2O adsorption on pristine surfaces of MS_2

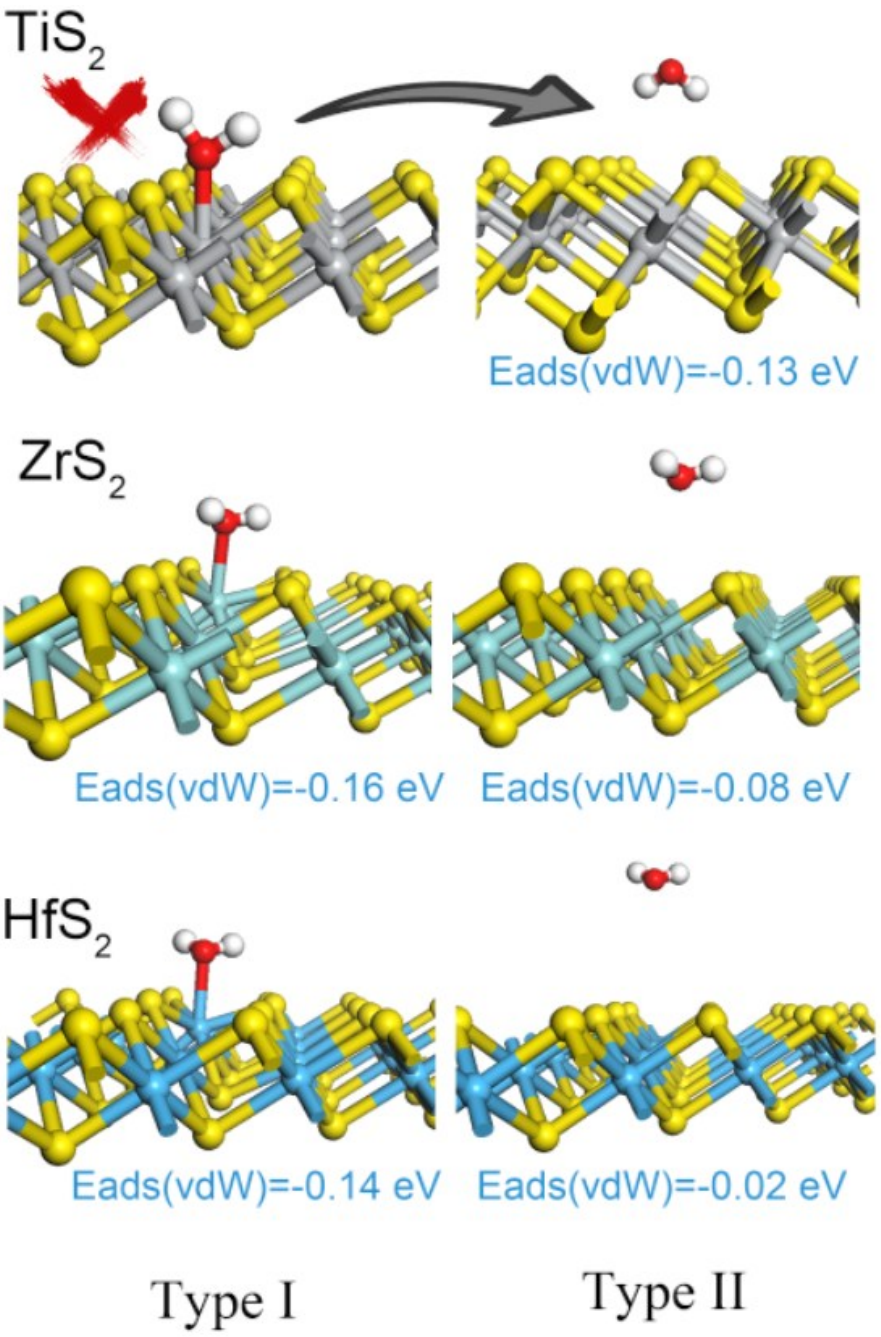

Figure S4. Adsorption structures and energies of H_2O on pristine MS_2 (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.

3.2 O_2 adsorption on pristine surfaces of MS_2

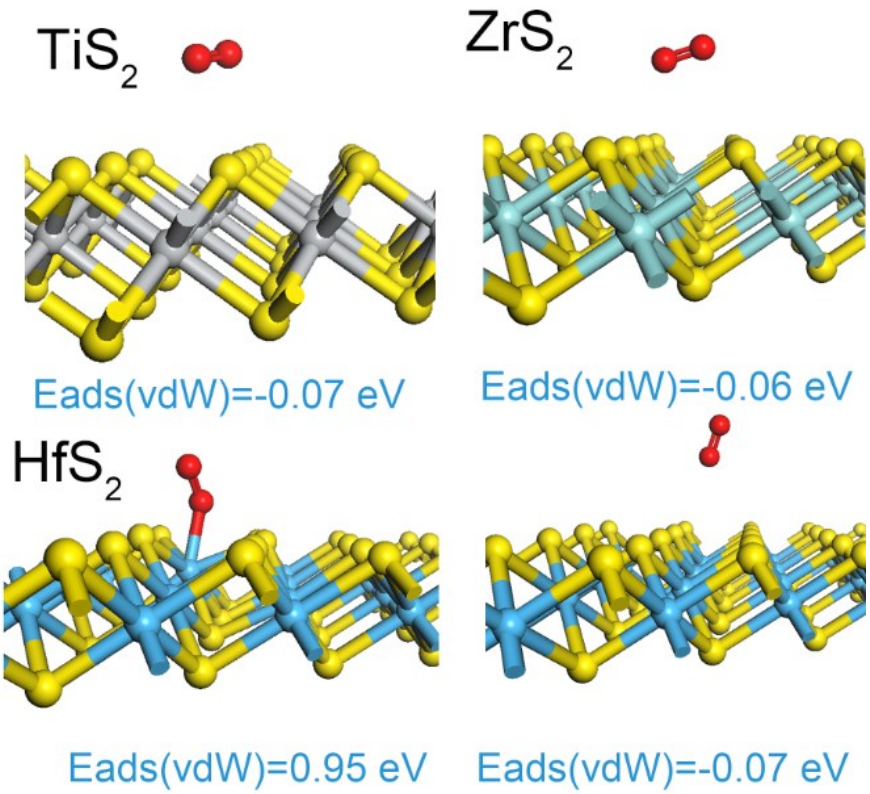

Figure S5. Adsorption structures and energies of O_2 on pristine MS_2 (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.

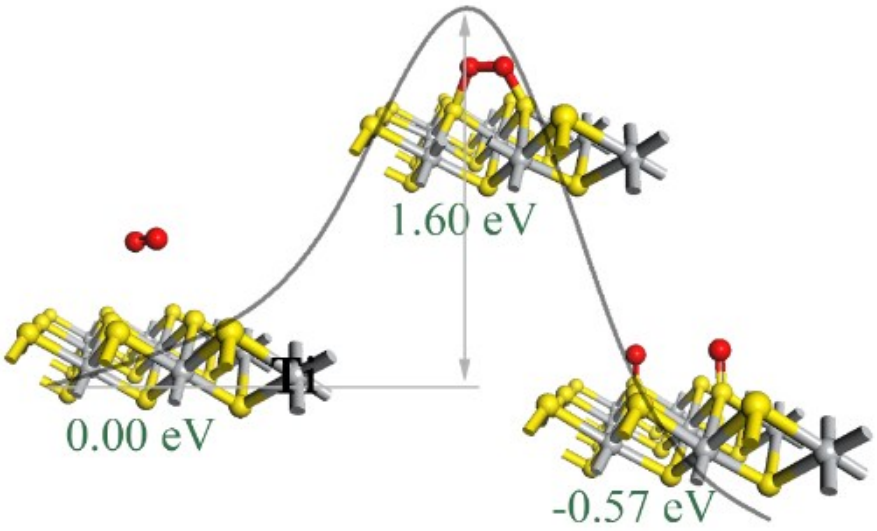

Figure S6. Direct surface oxidation on pristine TiS2 (001) surface, Ti, S and O are marked in grey, yellow and red respectively.

4. Sulfur vacancy

4.1 H_2O adsorption on sulfur vacancy sites of MS_2

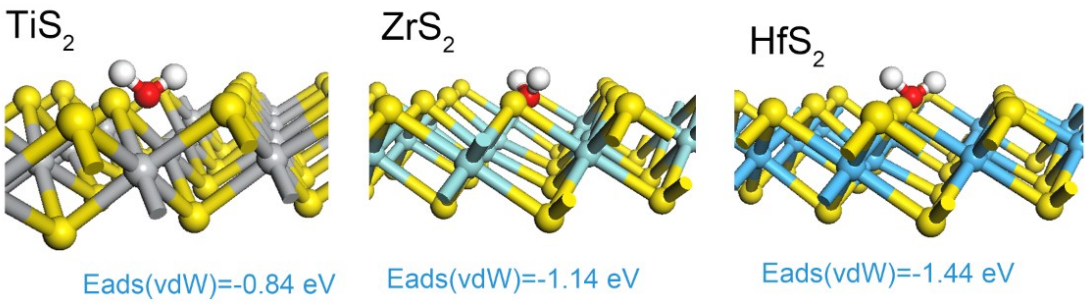

Figure S7. Adsorption structures and energies of H_2O on a sulfur vacancy site of MS_2 (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2.

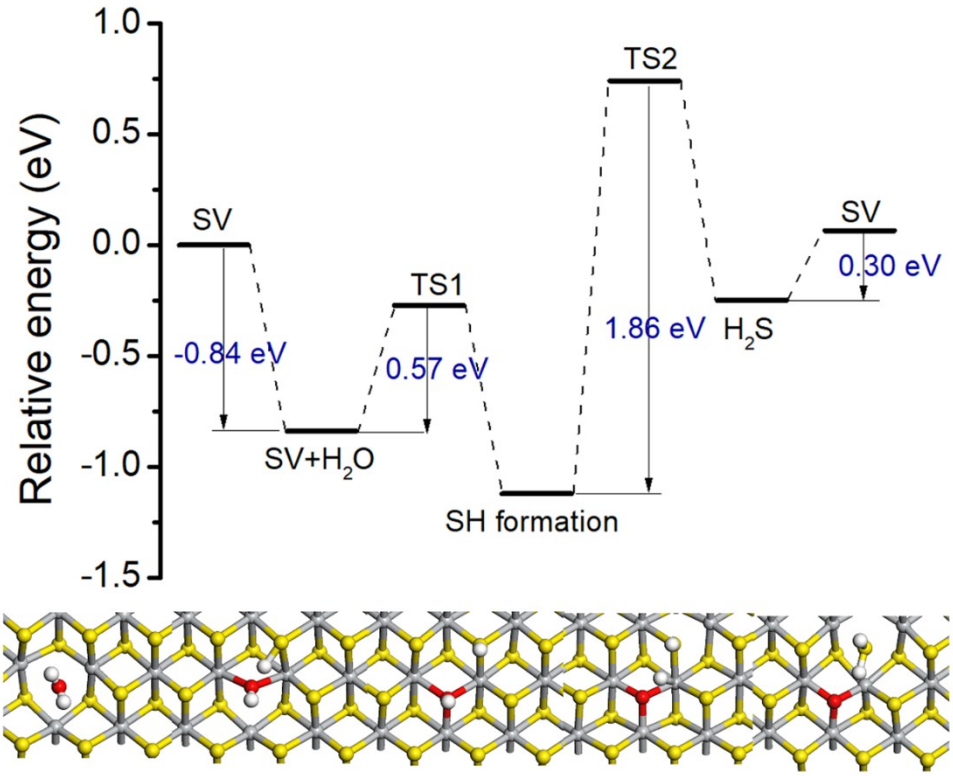

Figure S8. Proposed reaction pathway of water oxidation process at a TiS_2 surface vacancy site, the numbers in blue are calculated kinetic barriers for SH formation and H2S formation.

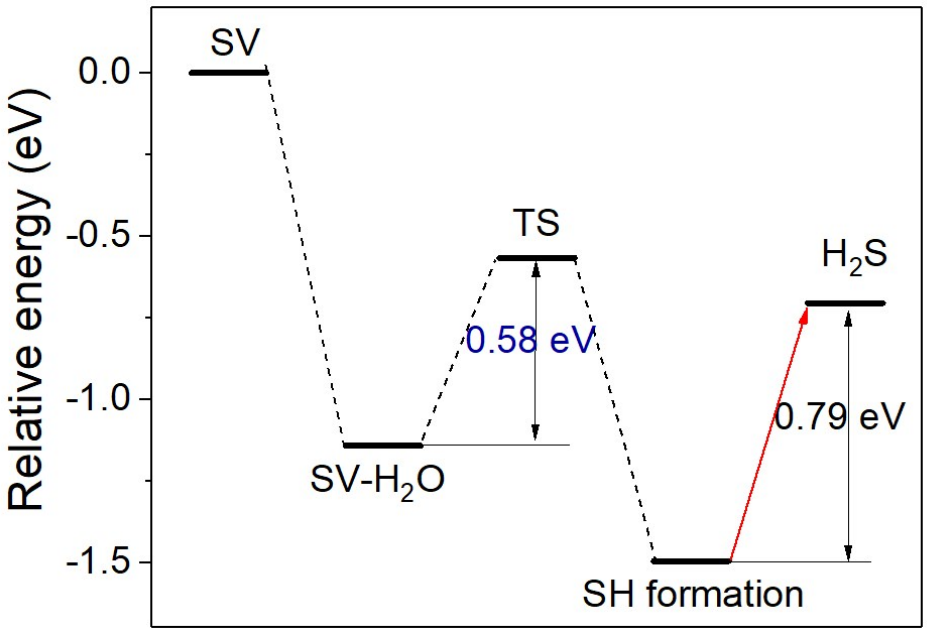

Figure S9. Proposed reaction pathway of water oxidation process at a ZrS_2 surface vacancy site. The number in blue is calculated kinetic barrier for SH formation. The formation of H2S is energy unfavorable by 0.79 eV. The structures are very similar with the case of HfS2 as shown in Figure 2b.

4.2 O_2 adsorption on sulfur vacancy sites of MS_2

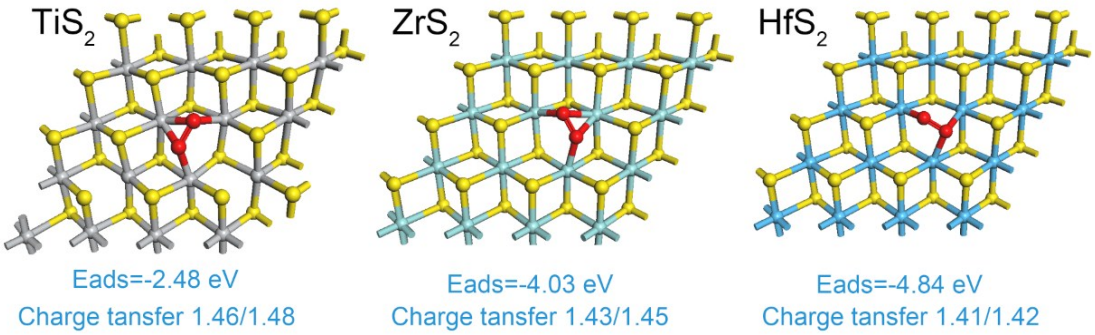

Figure S10. Adsorption structures and energies of O_2 on a sulfur vacancy site of MS_2 (001) (M=Ti, Zr and Hf) surfaces. The vdW corrections are used by PBE+D2. Charge transfer from O_2 to MS2 is analyzed by Bader charge analysis.

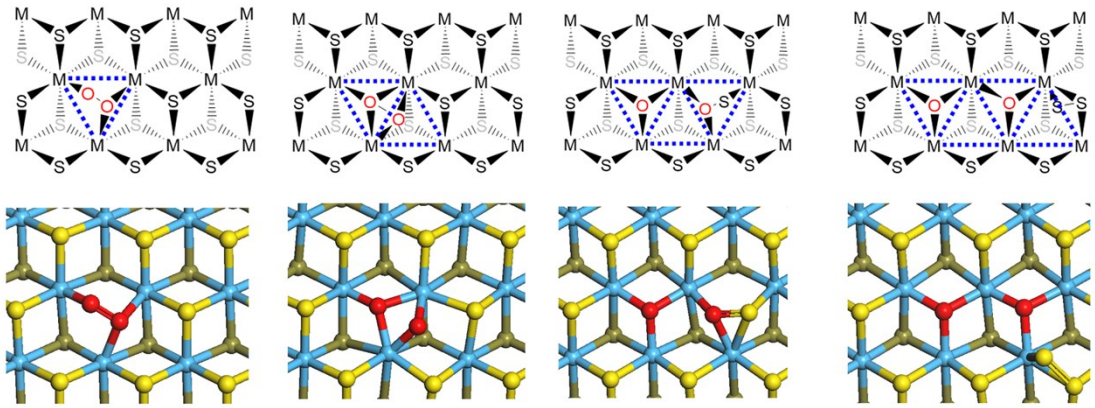

Figure S11. Structure evolution of O_2 adsorbed at a sulfur vacancy site. The structures shown in the Figure are examples from HfS_2, but can be applied to TiS_2 and ZrS_2 as well.

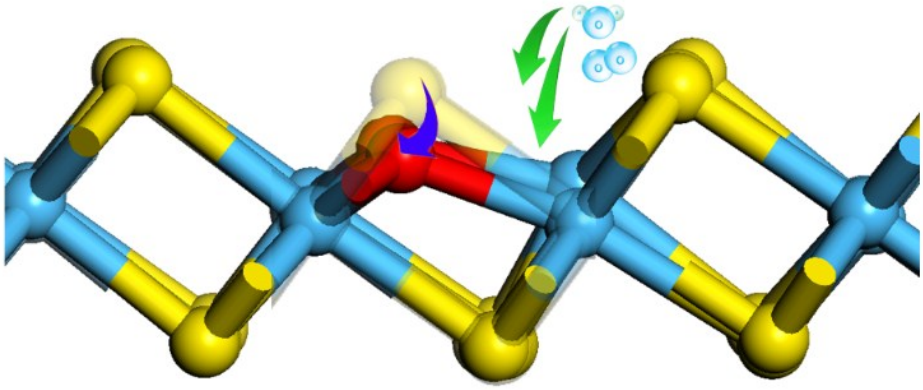

Figure S12. The shrink of lattice site into the inner part of the MS_2 comparing with initial S site (shadowed yellow) by O substitution, and O_2 and H_2O may attack these surrounding metals.

5. O-doped surface

5.1 O_2 and H_2O adsorption on O-doped HfS_2 and ZrS_2 surfaces

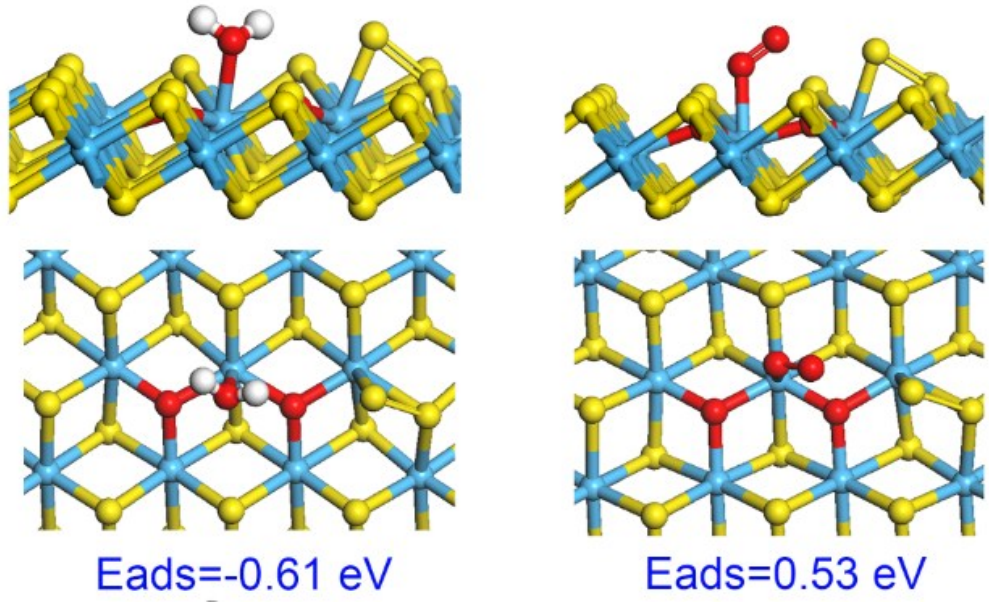

Figure S13. Side and top views of H_2O (left side) and O_2 (right side) adsorption on an O-doped HfS_2 surface.

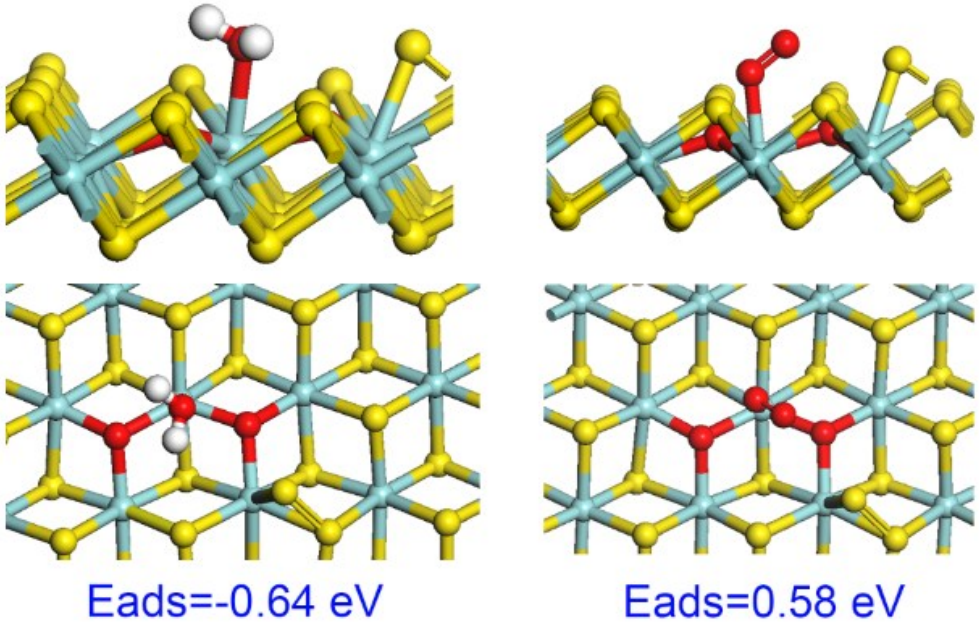

Figure S14. Side and top views of H_2O (left side) and O_2 (right side) adsorption on an O-doped ZrS_2

surface.

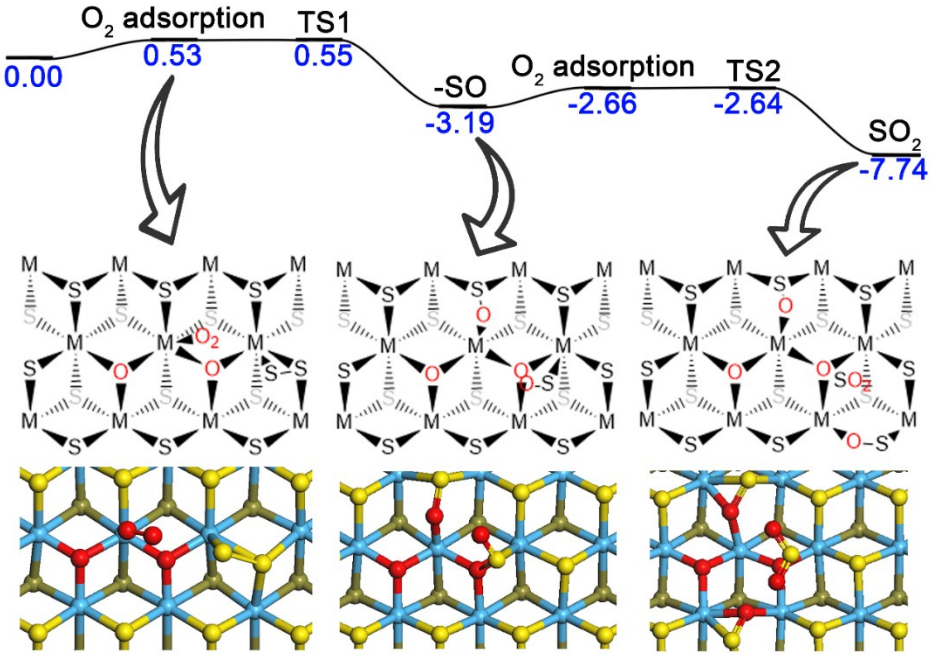

Figure S15. Proposed reaction pathway of O_2 induced oxidation on an O doped HfS2 surface.

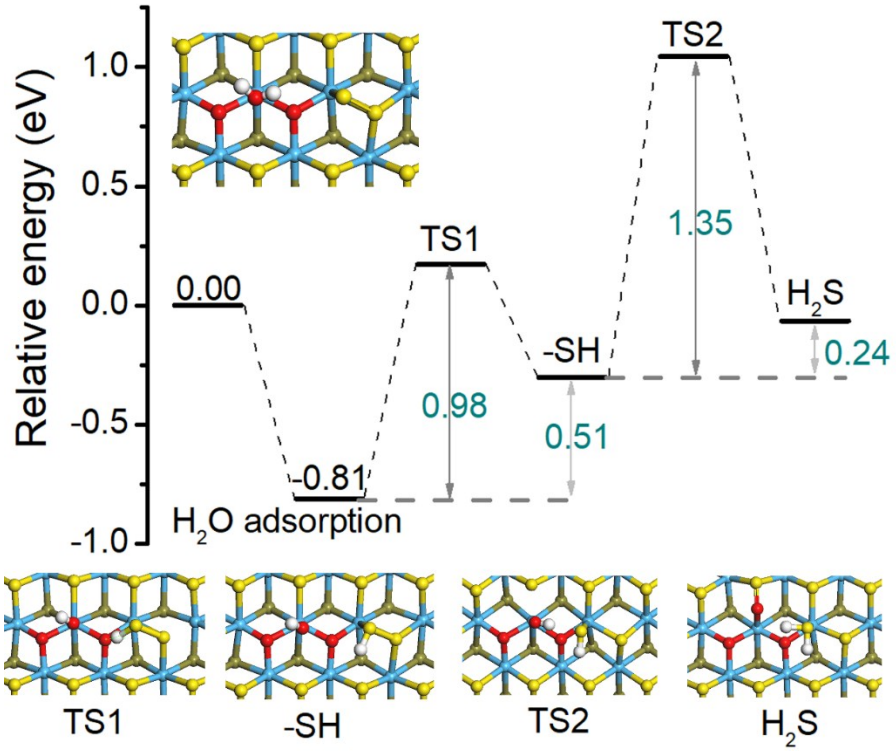

Figure S16. Proposed reaction pathway of H_2O induced oxidation on an O doped HfS_2 surface.

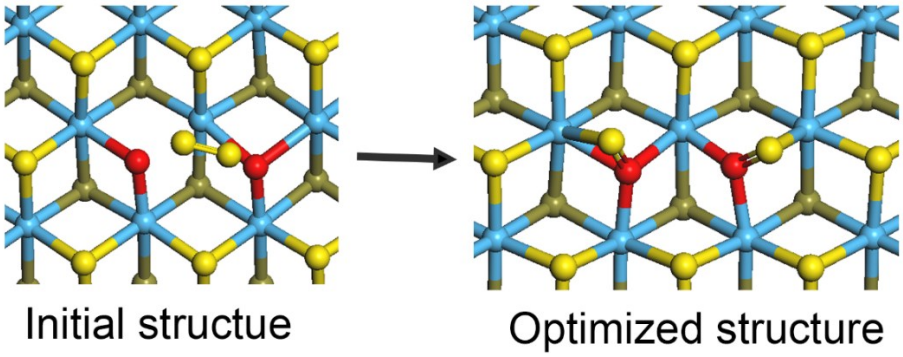

Figure S17. Geometry optimization of an S2 dimer on the O doped HfS_2 surface.

5.2 O-doped TiS_2 surface

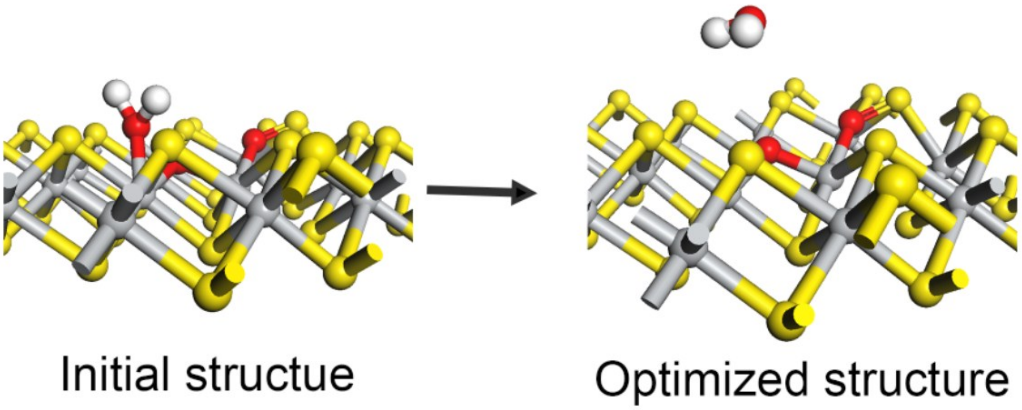

Figure S18. Geometry optimization of H_2O adsorption on an O doped TiS_2 surface and similar results can be found for non-polar O_2 adsorption.

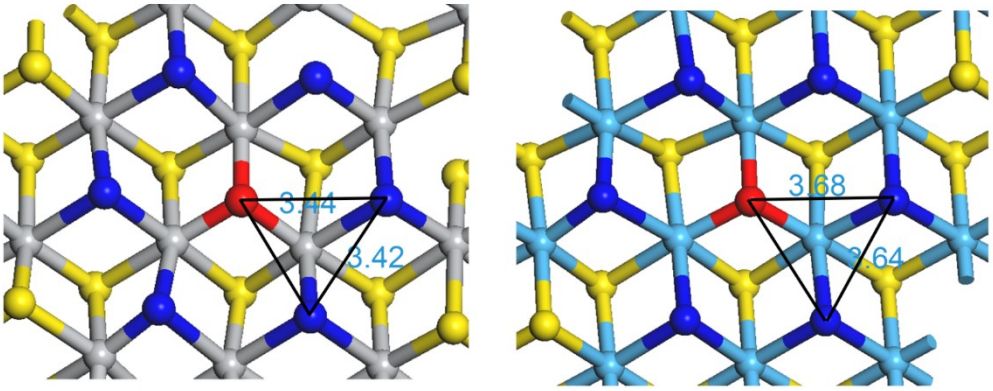

Figure S19. The steric effect on TiS_2 comparing with HfS_2, all the sulfur atoms surrounding the doped O are marked in blue. The units of distance are in Å.

6. Edges

6.1 H_2O adsorption on edge M sites of MS_2

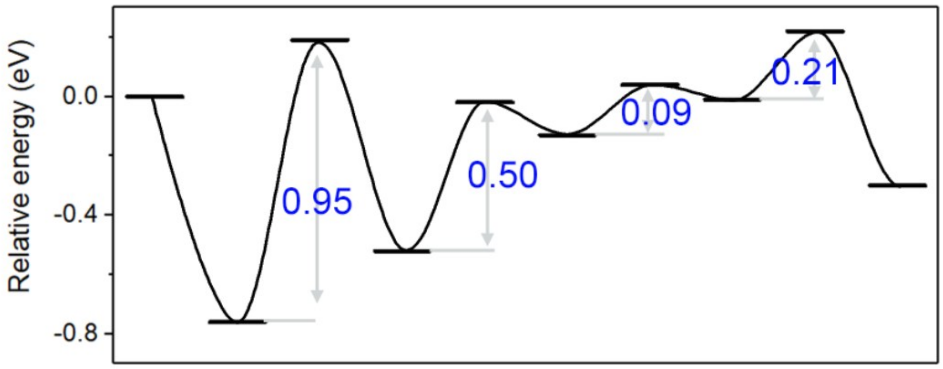

Figure 20. Proposed reaction pathways of H_2O induced oxidation at TiS_2 edge sites with 50% S coverage. The numbers denote for energy barriers of each step. All the energies and kinetic barriers are obtained from ref. 16 [*J. Phys. Chem. C* **2015**, 119, 15707].

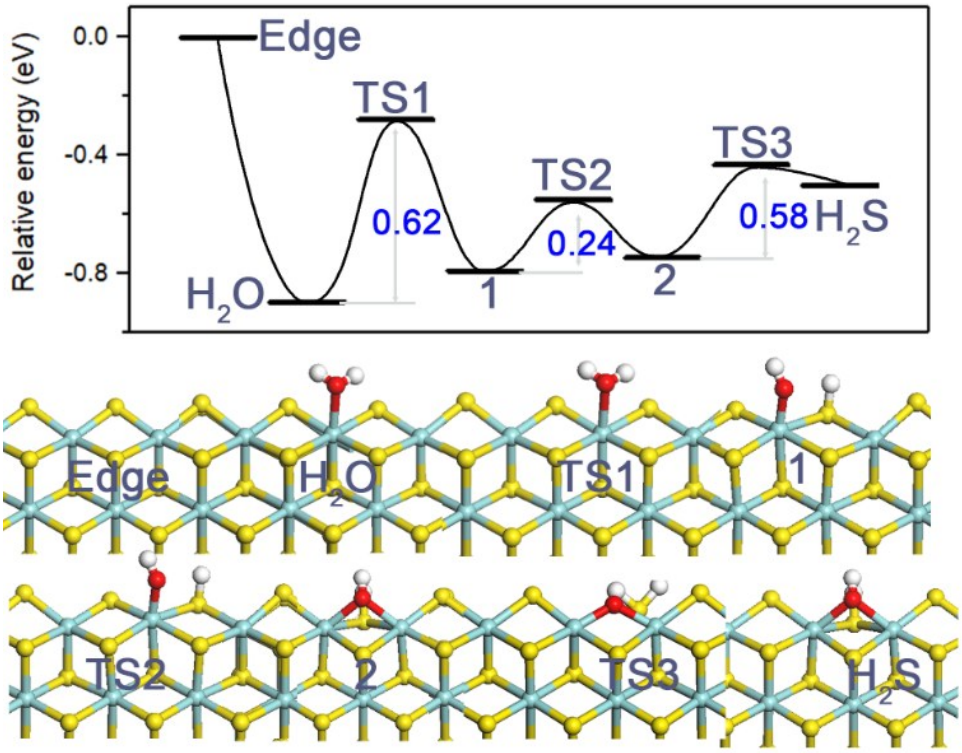

Figure 21. Proposed reaction pathways of H_2O induced oxidation at ZrS_2 edge sites with 50% S coverage. The numbers denote for energy barriers of each step.

6.2 O_2 adsorption on edge M sites of MS_2

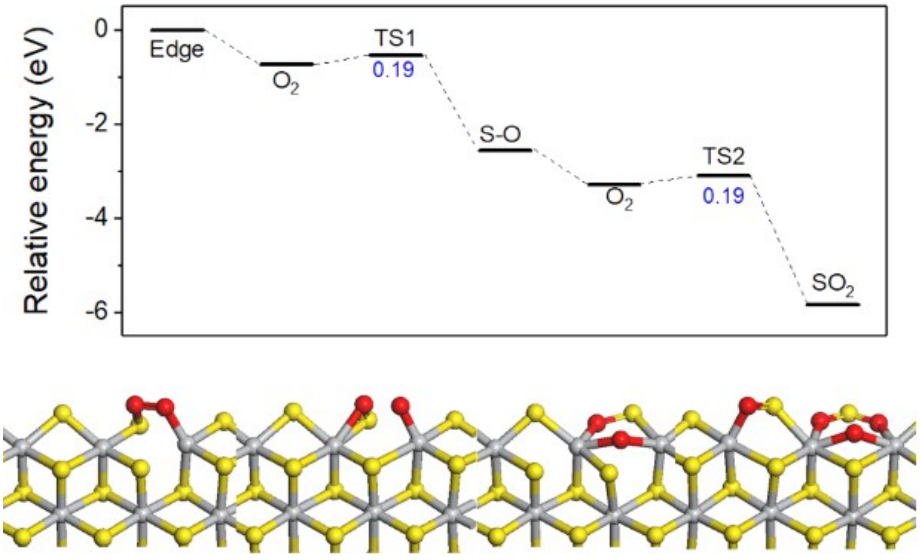

Figure 22. Proposed reaction pathways of O_2 induced oxidation at TiS_2 edge sites with 50% S coverage. The numbers denote for energy barriers of each step.

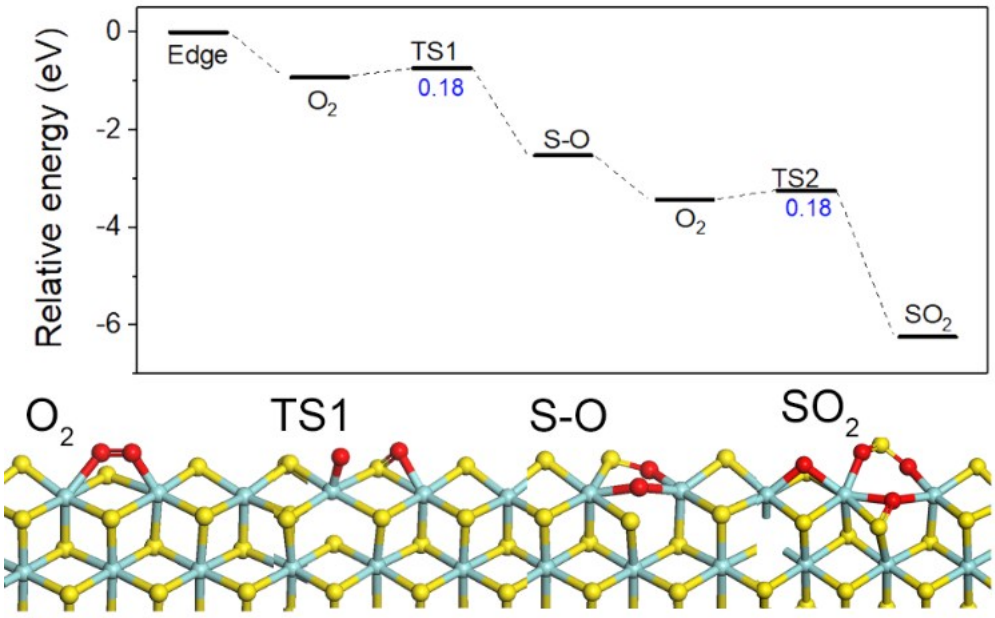

Figure 23. Proposed reaction pathways of O_2 induced oxidation at ZrS_2 edge sites with 50% S coverage. The numbers denote for energy barriers of each step.

6.3 Formation of TiO_x

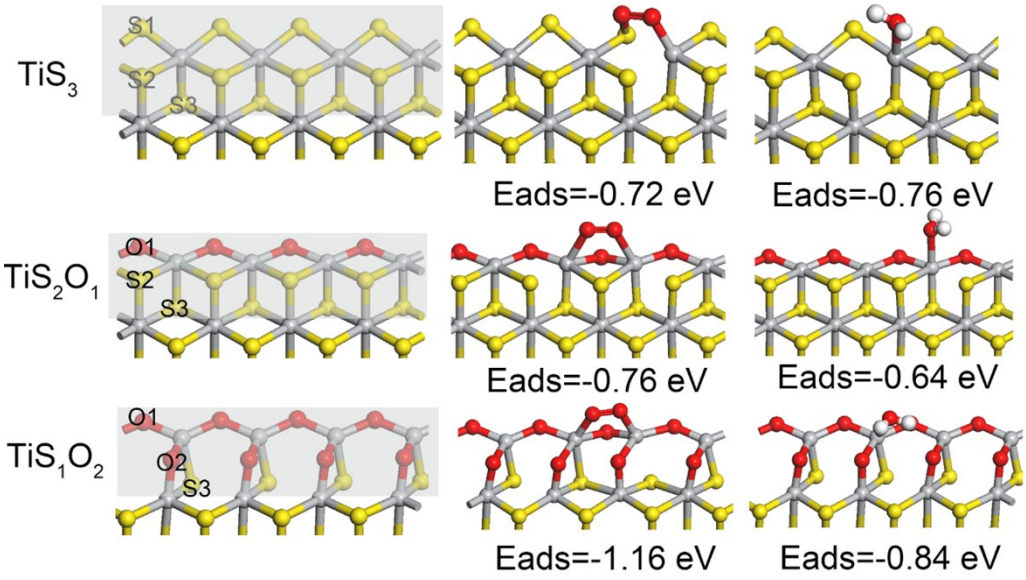

Figure 24. The adsorption of O_2 and H_2O at oxidized TiS_2 edge, the x ranges from 0-2, denotes as TiS_3, TiS_2O_1 and TiS_1O_2 respectively. The oxidized area is in shadow and TiO_3 can be seen in Figure 4 from the main text.

7. Appendix

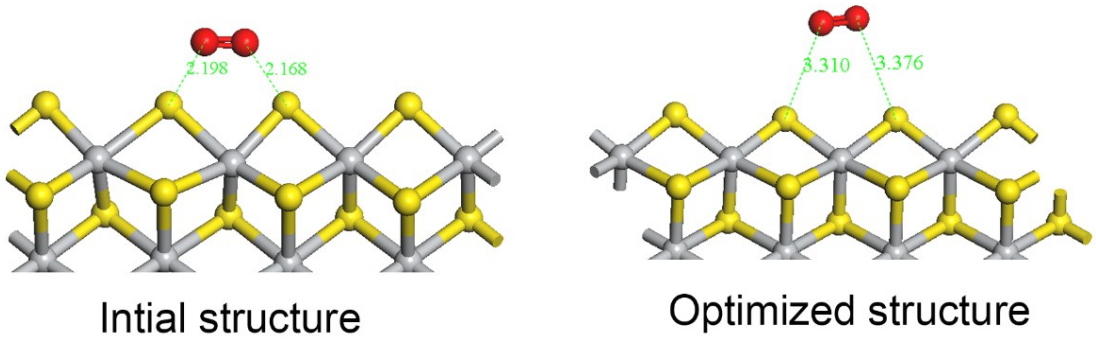

Figure 25. O_2 adsorption on TiS_2 S edge sites with 50% S coverage.

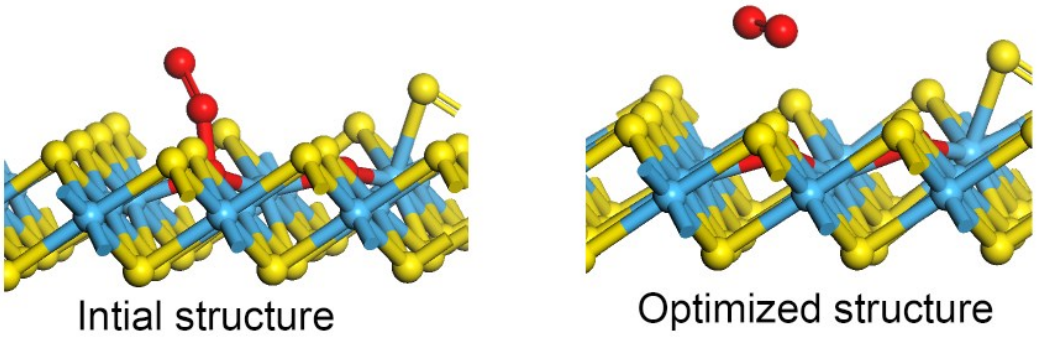

Figure 26. O_2 adsorption on an O-doped HfS_2 surface.

Table S1. Bond length of M-S in pristine MS_2, and M-O in O doped MS_2.

Bond length (Å)	M-S	M-O
Hf	2.55	2.10
Zr	2.57	2.13
Ti	2.45	1.98

Table S2. Adsorption energies of O_2 and H_2O on various sites of MS_2, units are in eV. Adsorption structures can be seen in each part of the supporting information.

	MS_2	O_2	H_2O
Pristine surface	TiS_2	-0.07	-0.06
	ZrS_2	-0.06	-0.16
	HfS_2	-0.07	-0.14
Sulfur vacancy	TiS_2	-2.48	-0.84
	ZrS_2	-4.03	-1.14
	HfS_2	-4.84	-1.44
O-doped surface	TiS_2	-0.07	-0.06
	ZrS_2	0.53	-0.61
	HfS_2	0.58	-0.64
edge	TiS_2	-0.72	-0.76
	ZrS_2	-0.92	-0.90
	HfS_2	-0.42	-1.11