Supplemental Information

Unraveling Energetics and States of Adsorbing Oxygen Species with MoS$_2$ for Modulated Work Function†

Hejin Yan[a], Hongfei Chen[a], Xiangyue Cui[a], Qiye Guan[a], Bowen Wang[a], Yongqing Cai[a*]

[a]Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Taipa, Macau, China

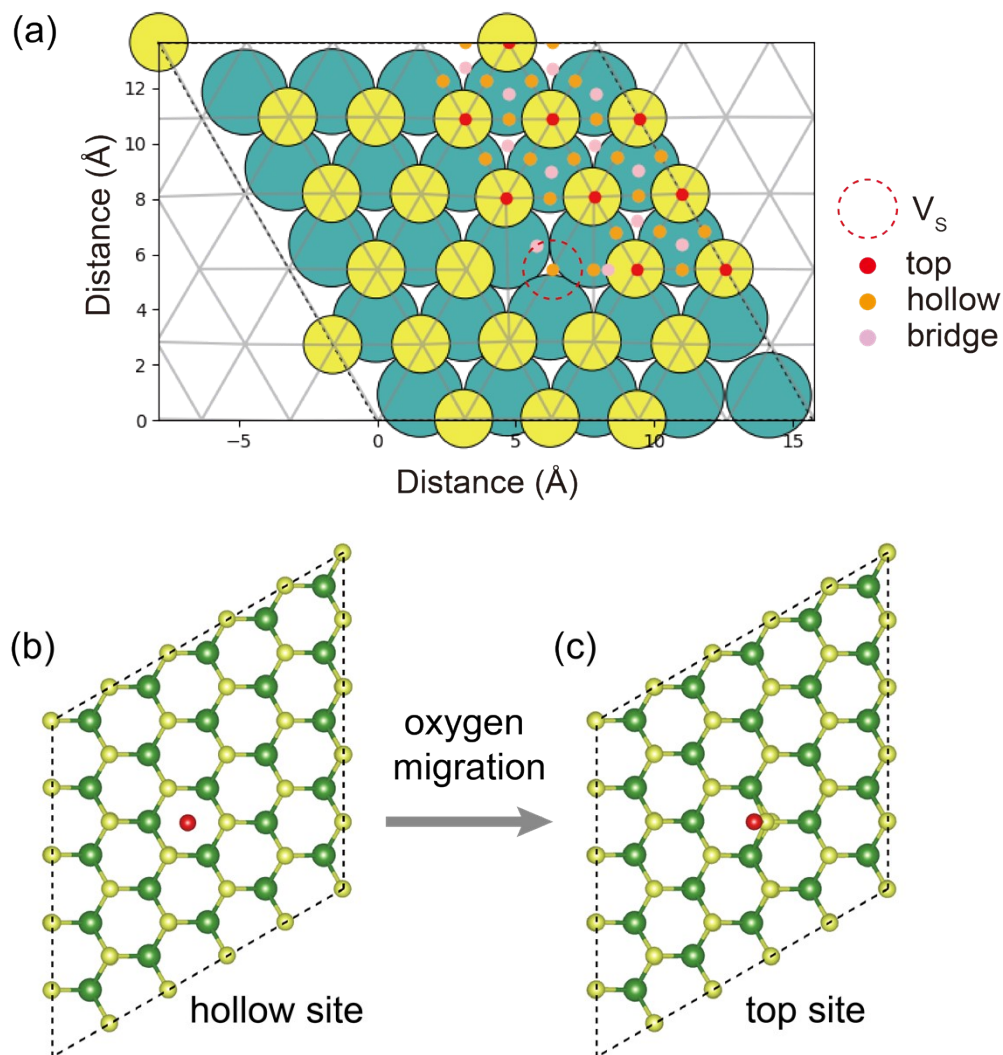*Corresponding Author

Yongqing Cai* E-mail: yongqingcai@um.edu.mo

Fig. S1 (a) Screened nonequivalent adsorption sites for adsorption on the V_S containing MoS_2 surface, including the top, hollow, and bridge sites. The hollow site adsorption of oxygen before (**b**) and after (**c**) structure optimization. The initial hollow site structure is unstable, and it converts to a top site adsorption.

Supplementary note: The ASE library is used to search for the nonequivalent adsorption sites on the V_S containing MoS_2 surface.[1, 2] There are 9 atop, 12 hollow, and 21 bridge sites in the model. In Fig. S1a, some sulfur atoms at the edge are missing due to periodic display, the V_S are marked by red dashed circle.
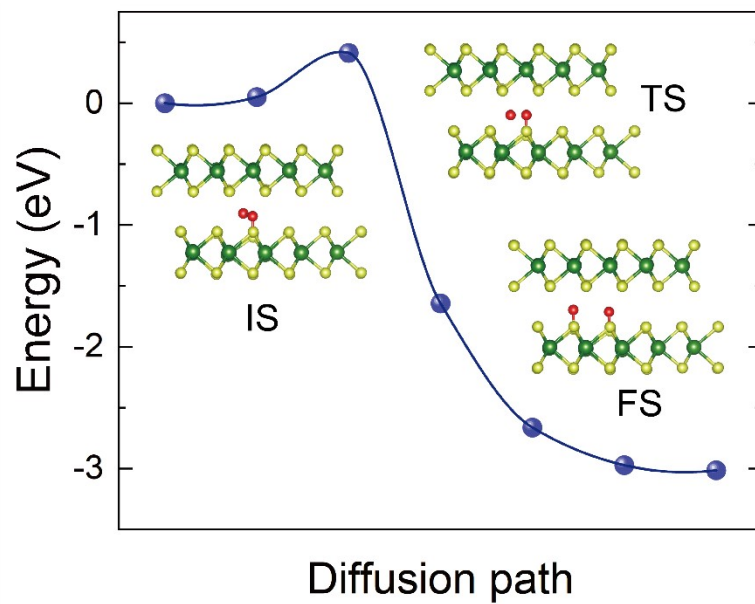
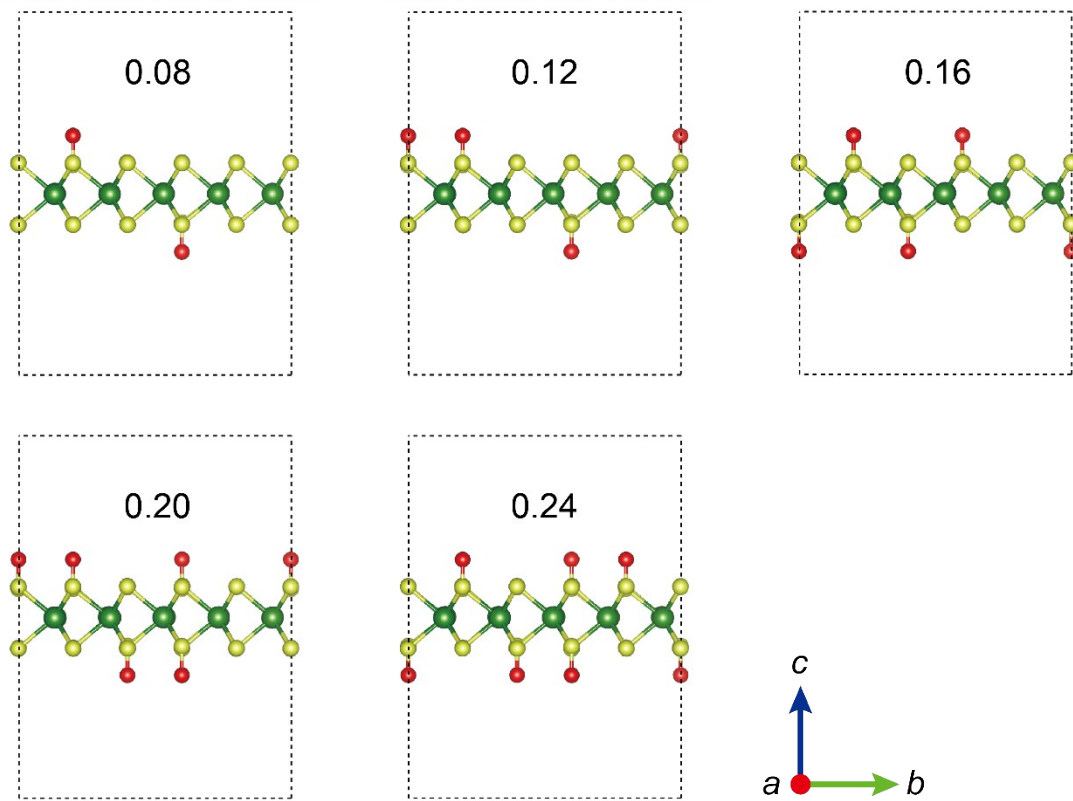**Fig. S2** Activation energy for oxygen dissociation within the vdWs gap of $O_{2(Sorb)}$.

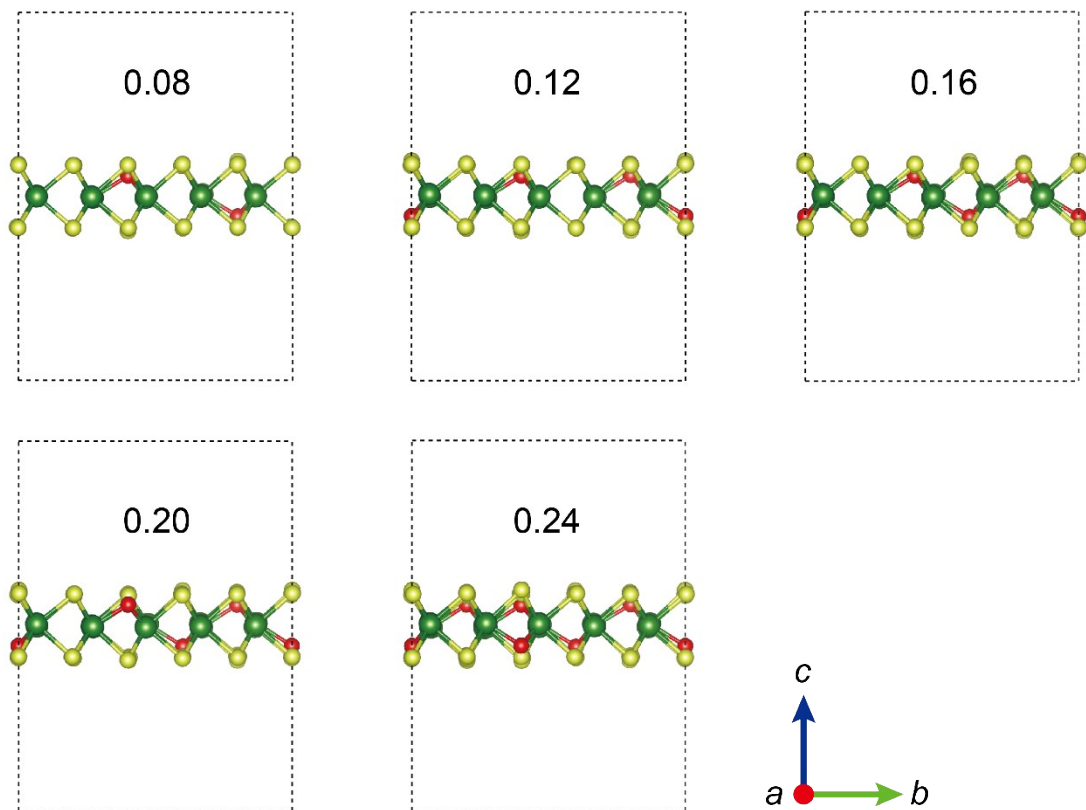**Fig. S3** Optimized structures of O_{Top} of different oxygen concentration for both facets situation.

Fig. S4 Optimized structures of O_S of different oxygen concentration for both facets situation.
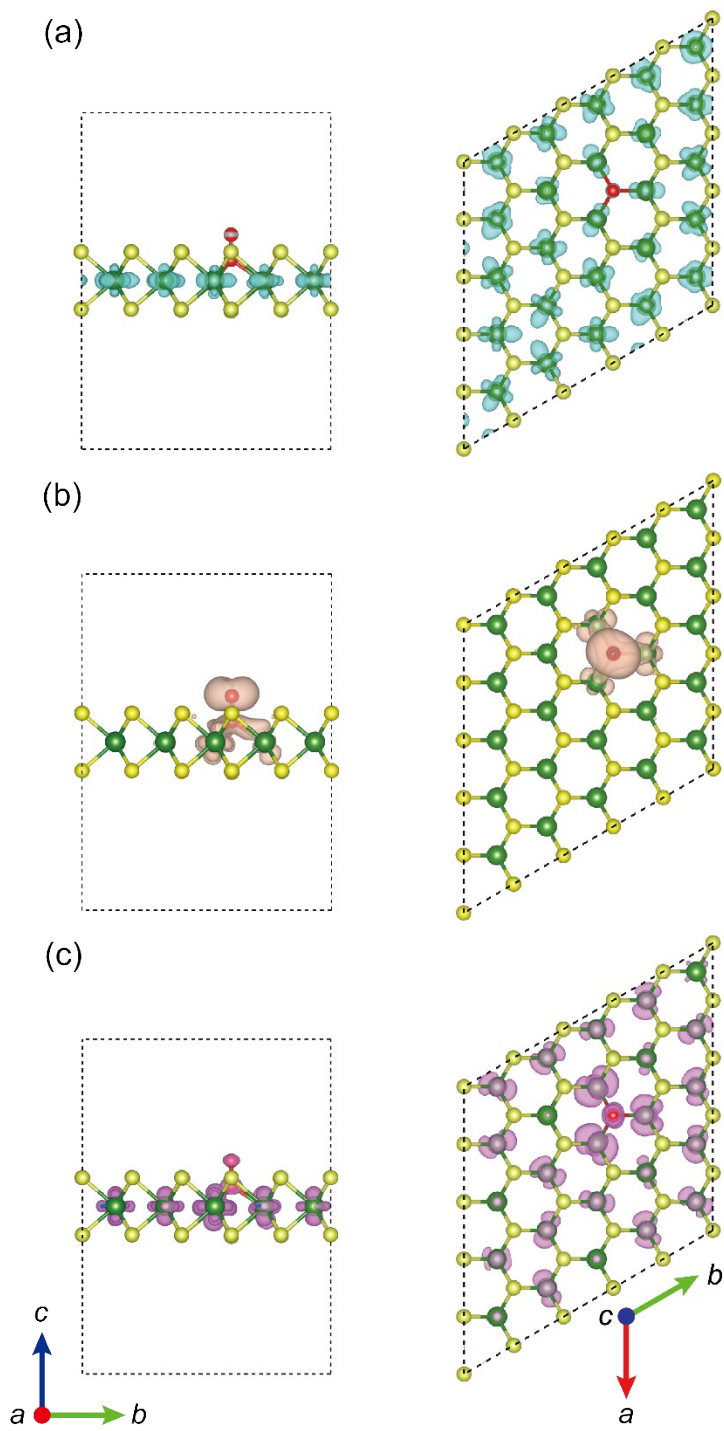
Fig. S5 Charge density distribution of (**a**) VBM, (**b**) in-gap states, and (**c**) CBM in $O_{2(Sub)}$ with an iso-surface of 1.5×10^{-3} e.
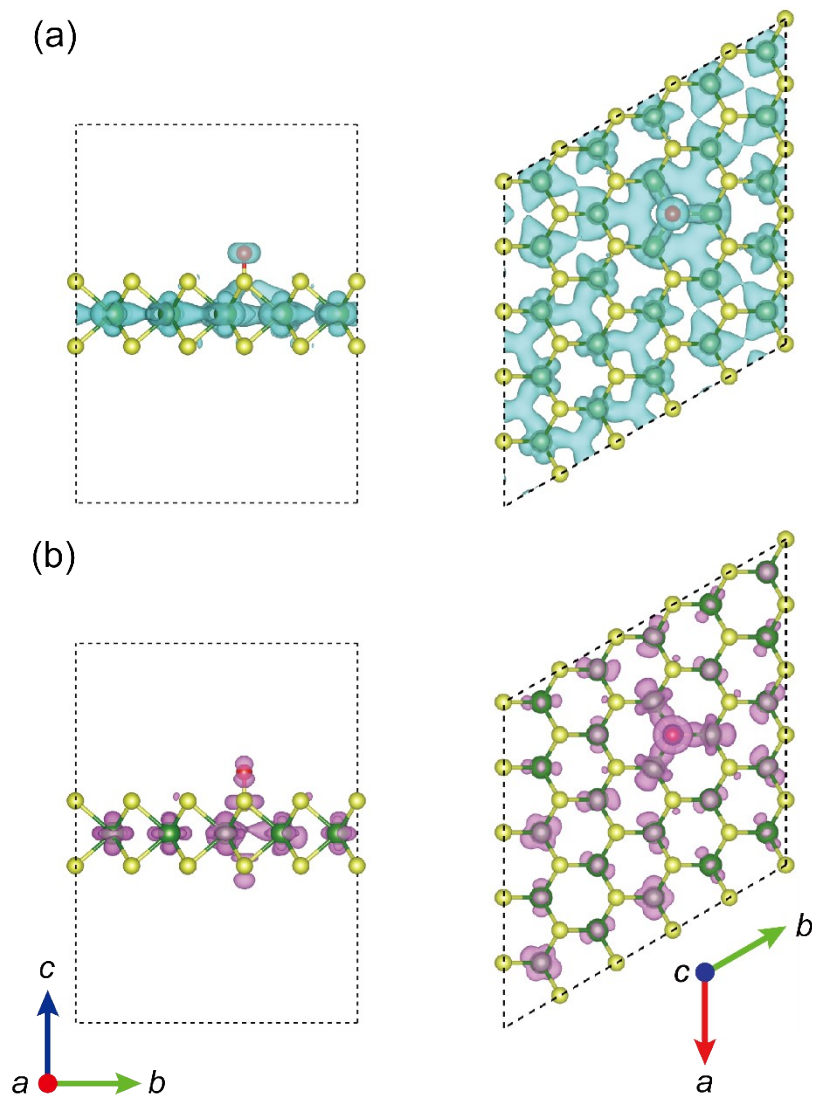
Fig. S6 Charge density distribution of (**a**) VBM and (**b**) CBM in O_{Top} with an iso-surface of 1.5 $\times$ 10^{-3} e.
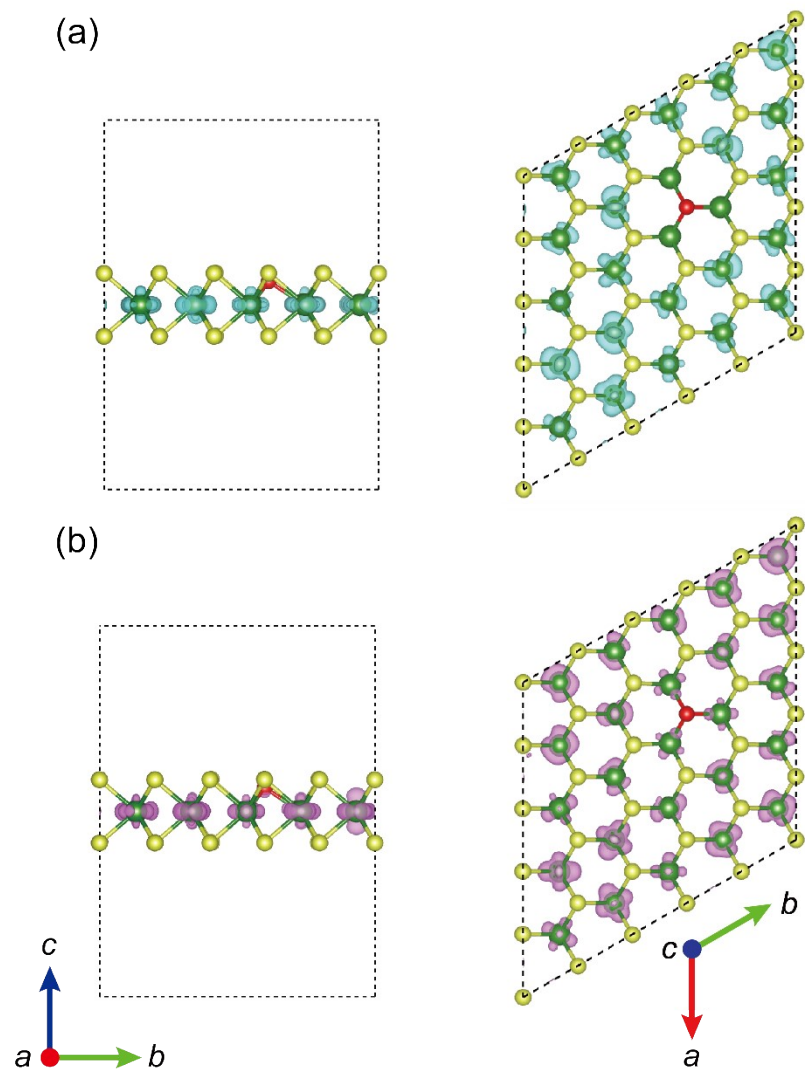
(a)

(b)

Fig. S7 Charge density distribution of (**a**) VBM and (**b**) CBM in O_S with an iso-surface of 1.5×10^{-3} e.
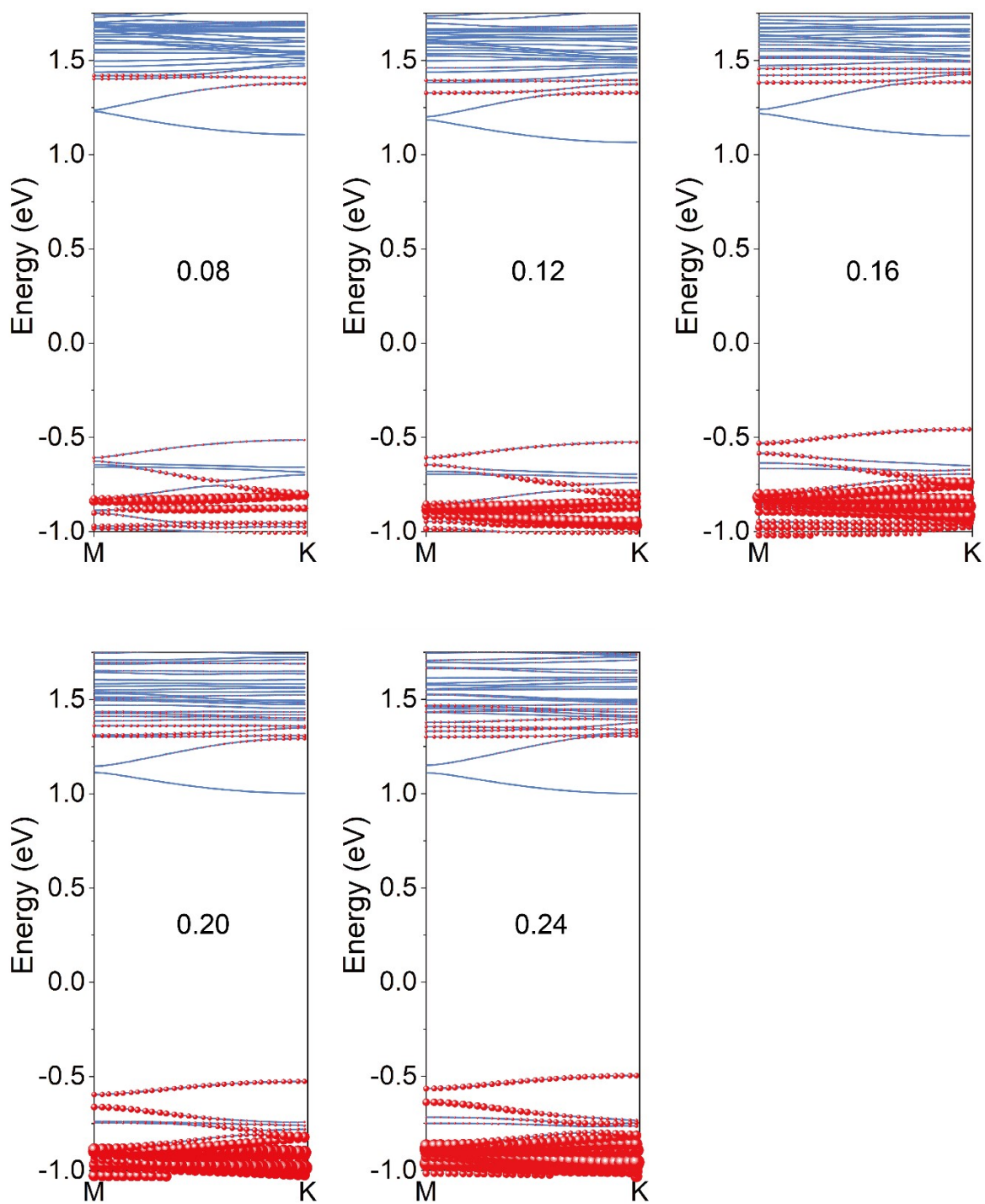
Fig. S8 Oxygen contribution projected band structures of O_{Top} of different oxygen concentration for both facets situation.
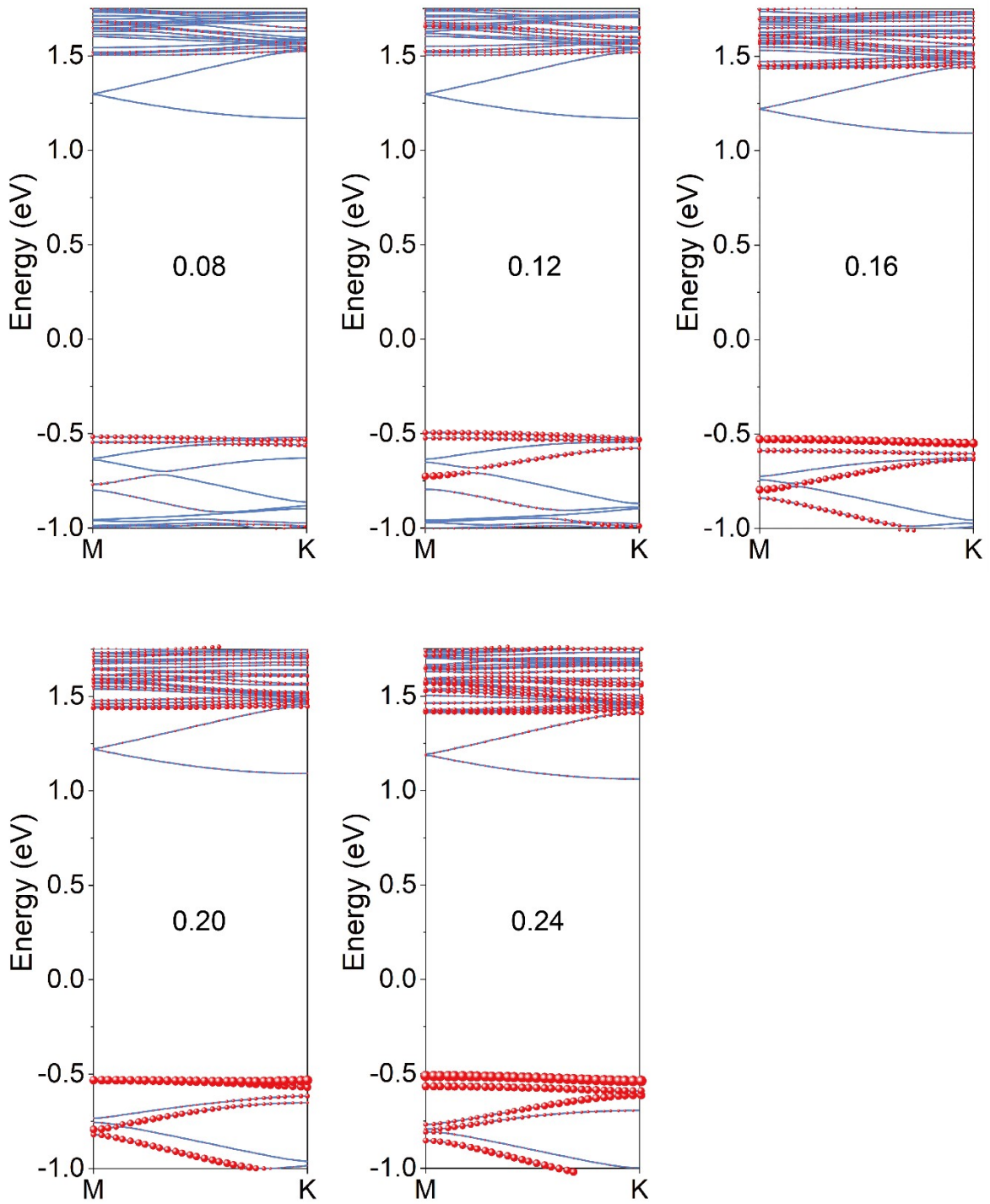
Fig. S9 Oxygen contribution projected band structures of O_S of different oxygen concentration for both facets situation.
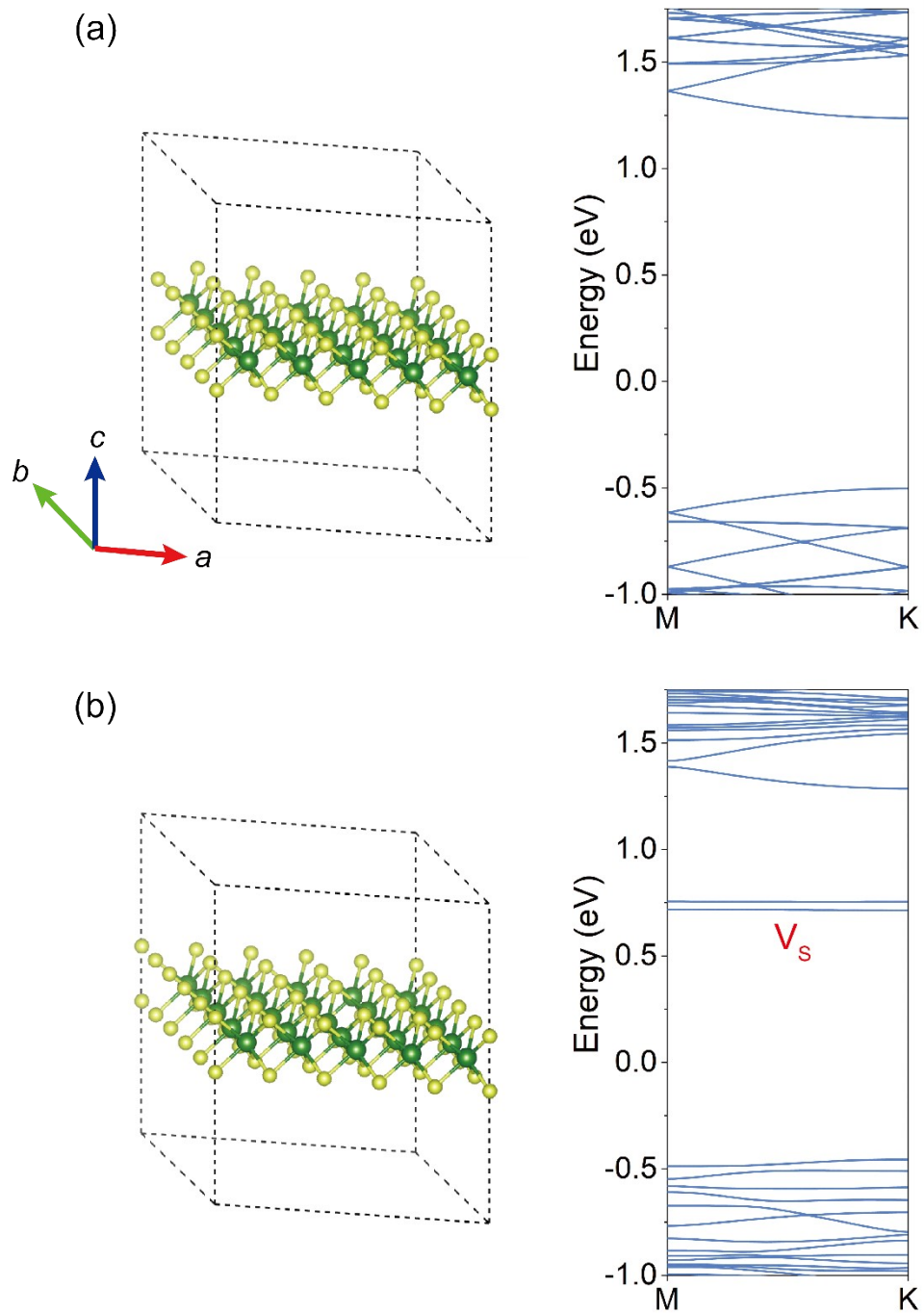
Fig. S10 Atomic structure and band structure of monolayer MoS_2 without (**a**) and with (**b**) V_S.

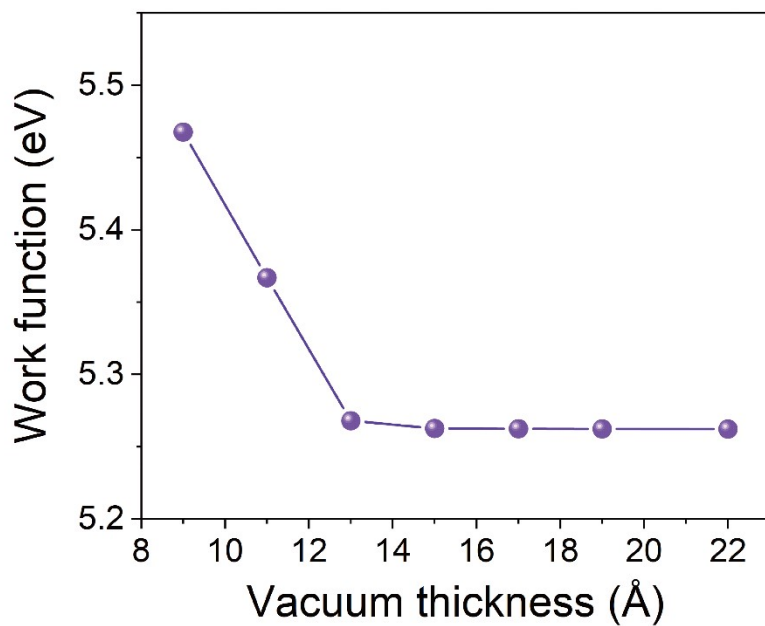Flat in-gap states exist in the case of V_S.

Fig. S11 Convergence test for the vacuum layer thickness dependent work function in MoS_2 monolayer.

Table S1 Formation energy for various O adsorbates on MoS_2 under S-poor ($\mu_{S,min}$) and S-rich ($\mu_{S,max}$) conditions.

Adsorbate type	Formation energy (eV)	
	$\mu_{S,min}$	$\mu_{S,max}$
$O_{2(Sorb)}$	1.72	1.72
$O_{2(Sub)}$	-1.03	0.26
O_{Top}	-1.17	-1.17
O_S	-3.24	-1.96

Table S2 Lattice parameters of O_{Top} of different oxygen concentration for both facets situation.

Oxygen concentration	a (Å)
0.08	15.93490
0.12	15.94300
0.16	15.95240
0.20	15.96030
0.24	15.97134

Table S3 Lattice parameters of O_S of different oxygen concentration for both facets situation.

Oxygen concentration	a (Å)
0.08	15.83550
0.12	15.79550
0.16	15.75520
0.20	15.71490
0.24	15.67670

References:

1. A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dułak, J. Friis, M. N. Groves, B. Hammer and C. Hargus, *J. Phys.: Condens. Matter*, 2017, **29**, 273002.
2. Z. Zhang, Z.-H. Cui, E. Jimenez-Izal, P. Sautet and A. N. Alexandrova, *ACS Catal.*, 2020, **10**, 13867-13877.