Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information: Origin of hydrogen evolution activity on MS_2 (M = Mo or Nb) monolayers

Xiaobo Chen,*[a] Yu Gu,[a] Guohua Tao,[b] Yanli Pei,[c] Guangjin Wang,[d] and Ni Cui[a]

[a]Department of Physics and Siyuan Laboratory, College of Science and Engineering, Jinan University, Guangzhou 510632, China.

[b]Shenzhen Key Laboratory of New Energy Materials by Design, Peking University, Shenzhen 518055, China.

[c]State Key Lab of Optoelectronics Materials & Technologies, School of Physics & Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

[d]College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan 432000, China.

Corresponding author: txbchen@jnu.edu.cn

1. Data for verification of the PES method

Table S1. Total energies for a 1H-NbS_2 monolayer ($E(Mo_{10}S_{30})$) and its hydrogenated counterpart ($E(Mo_{10}S_{30}H)$) with 1/8 H coverage. ΔE_H is calculated using Eq. (1). E'_{ea} and E'_{pa} are calculated by Eq (4) and (5), respectively. $E_{A\rightarrow E}$ can be calculated according to $E_{A\rightarrow E} = -(E_{ea} + \varepsilon_{ea} + E_{pa} + \varepsilon_{pa})$. For quantitatively verifying the PES model in the text, all the data are shown with 6 numbers after their decimal points.

$E(Nb_8S_{16})$	$E(Nb_8S_{16}H_1)$	E'_{ea}	E'_{pa}	$E_{A\rightarrow E}$	ΔE_H
-171.179022	-174.827780	2.021781	1.626977	-3.648758	-3.64827

The difference between $E_{A\rightarrow E}$ and ΔE_H is only -0.000488 eV, indicating they are numerically equivalent. This small difference is exactly equal to E(H), *i.e.* the deviation of the VASP-calculated H atom energy from the atomic reference energy of H. As will be indicated in Table S2, E(H) reflects the accuracy of the pseudopotential.

2. Data for ΔG calculations

Table S2. Total energies for a isolated H atom E(H), a H atom in gas molecular state ($E(H_2)/2$), and their difference ΔE_{cp}. E_{ZPE}(gas) and E_{ZPE}(ads) are the zero point energies of a H atom in gas molecular state and adsorbed state, respectively. The calculated E_{ZPE}(gas) is 0.145 eV, in agreement with the experimental value of 0.135 eV.[1] $T\Delta S_H$ is obtained from the literature.[1]

	E(H)	$E(H_2)/2$	ΔE_{cp}	E_{ZPE}(gas)	E_{ZPE}(ads)	$T\Delta S_H$	$\Delta E_{ZPE} - T\Delta S_H$
1H-MoS_2					0.102		0.161
1T-MoS_2					0.098		0.157
	-0.000488	-3.380413	3.380	0.145		-0.205	
1H-NbS_2					0.093		0.152
1T-NbS_2					0.083		0.143

Note that all the total energies in Table S1 are calculated with respect to the atomic energies in reference configuration (*i.e.* the configuration for which the pseudopotential is generated). Consequently, E(H) should be as small as possible. The small value of -0.000488 eV for E(H) indicates the high accuracy of the PAW potential. In addition, it is seen that E_{ZPE}(ads) is weakly dependent on different materials.

Table S3. Structural parameters for the unit cells of all the monolayers. *a* and *b* are calculated in-plane lattice parameters. *T* is the vertical separation between S layers. M-S and M-M are distances between the corresponding atoms in MS_2. Previous calculation (Calc.) and experimental (Exp.) references are also included for comparison.

	a	*b*	*T*	M-S	M-M
1H-MoS_2	3.19		3.13	2.42	3.19
Exp.[2]	3.16		3.17	2.42	3.16
Calc.[3]	3.12		3.11	2.38	
1T-MoS_2	3.22	5.79	3.47	2.53, 2.50, 2.44, 2.41,	2.81, 3.85
Exp.[4]	3.22	5.68			
1H-NbS_2	3.36		3.14	2.49	3.36
Calc.[5]	3.35		3.14	2.49	
1T-NbS_2	3.39		3.09	2.49	3.39

The experimental data from Ref. 2 are for the bulk 2H-MoS_2.

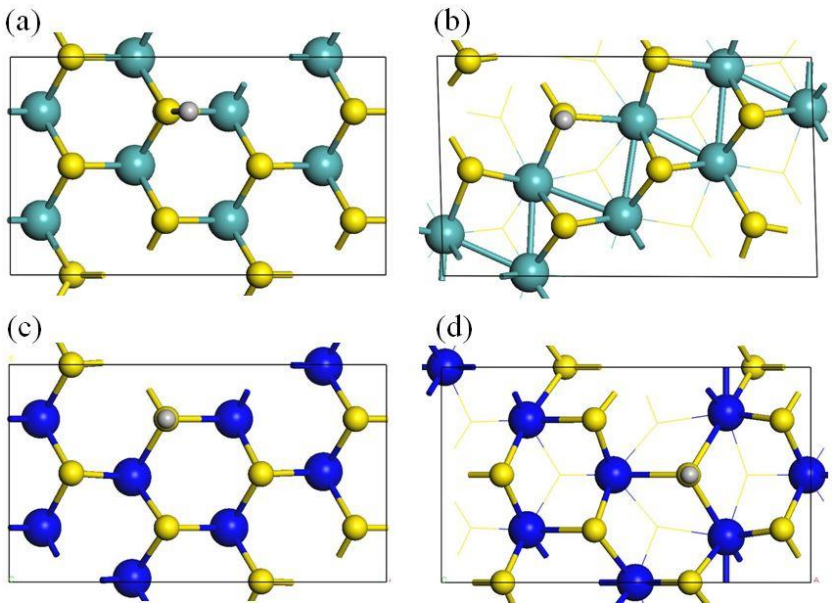

Figure S1. Top view of optimized structures for hydrogenated (a) 1H-MoS_2, (b) 1T-MoS_2, (c) 1H-NbS_2, and (d) 1T-NbS_2 monolayers. All the monolayers are in the *x*-*y* plane. Mo, Nb, S and H atoms are indicated by green, blue, yellow and grey balls, respectively.

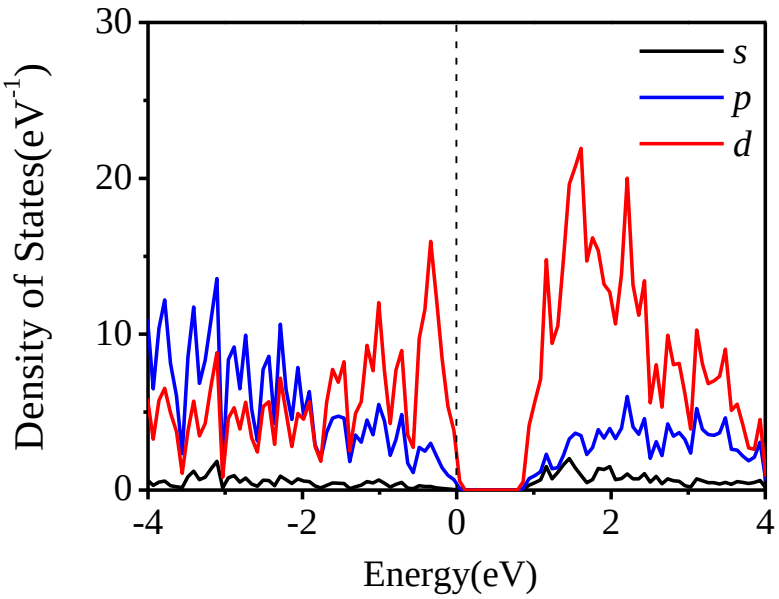

Figure S2. Projected density of states for 1T-MoS_2 with 100% H coverage. *s*, *p*, and *d* states are indicated by black, blue and red curves, respectively. The Fermi level is indicated by the dotted line.

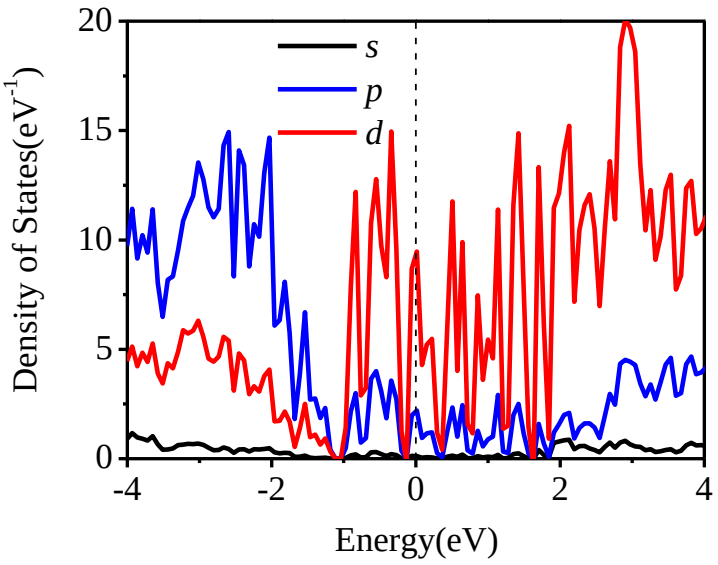

Figure S3. Projected density of states for 1T-NbS_2 with 75% H coverage. *s*, *p*, and *d* states are indicated by black, blue and red curves, respectively. The Fermi level is indicated by the dotted line.

REFERENCES

1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23-J26.
2. B. Schönfeld, J. J. Huang and S. C. Moss, *Acta Cryst. B*, 1983, **39**, 404-407.
3. T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu and J. Feng, *Nat Commun*, 2012, **3**, 887.
4. R. A. Gordon, D. Yang, E. D. Crozier, D. T. Jiang and R. F. Frindt, *Phys. Rev. B*, 2002, **65**, 125407.
5. Y. Zhou, Z. Wang, P. Yang, X. Zu, L. Yang, X. Sun and F. Gao, *ACS Nano*, 2012, **6**, 9727-9736.