Supporting Information

Mechanism of highly-enhanced hydrogen storage by two-dimensional 1T' MoS_2

Junyu Chen [a], Jiamu Cao [a,b,*], Jing Zhou [a,*], Yufeng Zhang [a,b,*], Mingxue Li [a], Weiqi Wang [a], Junfeng Liu [a], Xiaowei Liu [a,b]

[a]*MEMS Center, Harbin Institute of Technology, 150001, China.*

[b]*Key Laboratory of Micro-systems and Micro-Structures Manufacturing, Ministry of Education, 150001, China.*

*corresponding author

E-mail: caojiamu@hit.edu.cn (J.M. Cao)

E-mail: daxiongmao@hit.edu.cn (J. Zhou)

E-mail: yufeng_zhang@hit.edu.cn (Y.F. Zhang)

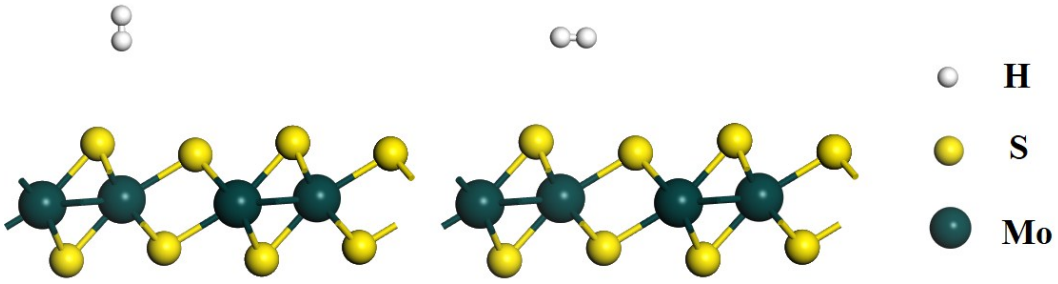

Figure S1. Adsorption forms of hydrogen molecules (a) vertically to the materials plane (b) horizontally to the materials plane

Figure S1 shows the two forms of hydrogen adsorbed on the surface of the materials. The adsorption positions were set on the basis of on hydrogen atom in the hydrogen molecule; and the origin distance between the benchmarking hydrogen atom and the centroid of the upper S atoms were fixed as 3 Å. We can also call the two forms of adsorption as edge on (vertically) and side on (horizontally)[1].

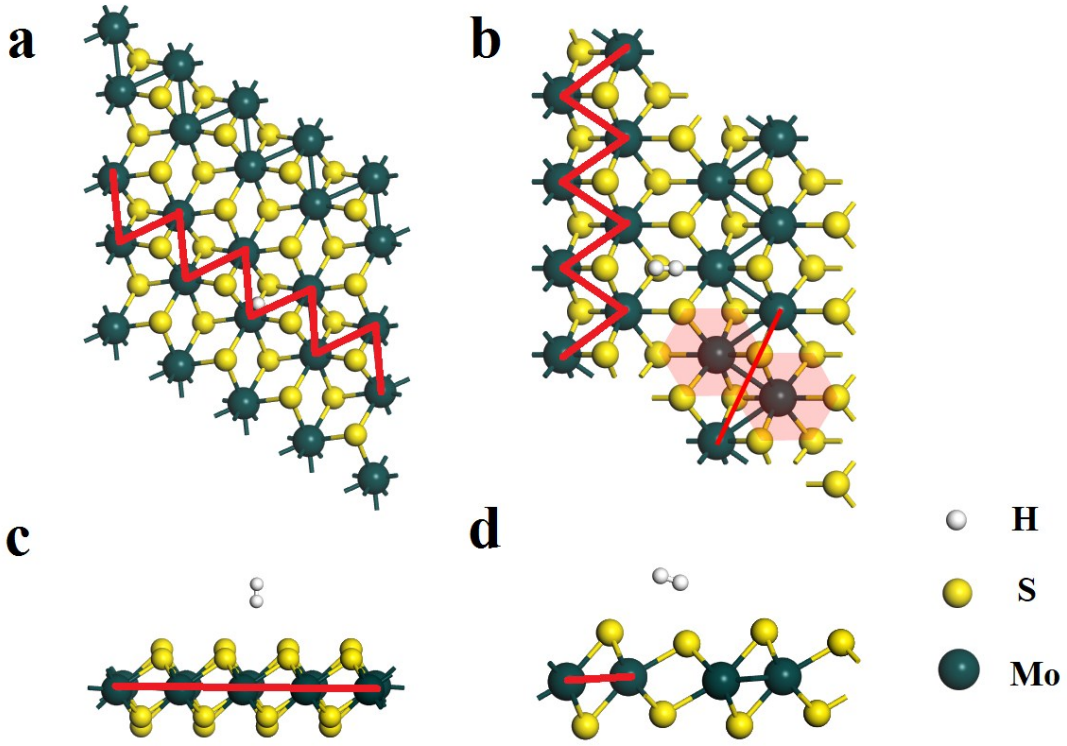

Figure S2. The most stable position of hydrogen molecule adsorbed on (a) and (c) pristine1T-phase MoS_2, (b) and (d) pristine 1T'-phase MoS_2

Figure S2 shows the situations of single hydrogen molecule adosrbed on the 1T or 1T'

MoS_2 that has the largest adsorption energy. Namely the cases that the acting forces between the hydrogen molecules and materials are the strongest[2]. For 1T MoS_2, it is above the middle of Mo atom and lower layer S atom, and the hydrogen did not move much after optimization. But the structure of MoS_2 changes a lot, similar to 1T' MoS_2, there are Mo-Mo bonds between every two rows of Mo atoms. This also adds to the change of the total energy, and it will make the adsorption energy results to be inaccurate. So, this method cannot calculate the adsorption energy when hydrogen molecules adsorbed on 1T MoS_2. But for the 1T' MoS_2, the structure was hardly changed, the energy change after geometry optimization are mostly adsorption energy. Thus, the study can be carried out.

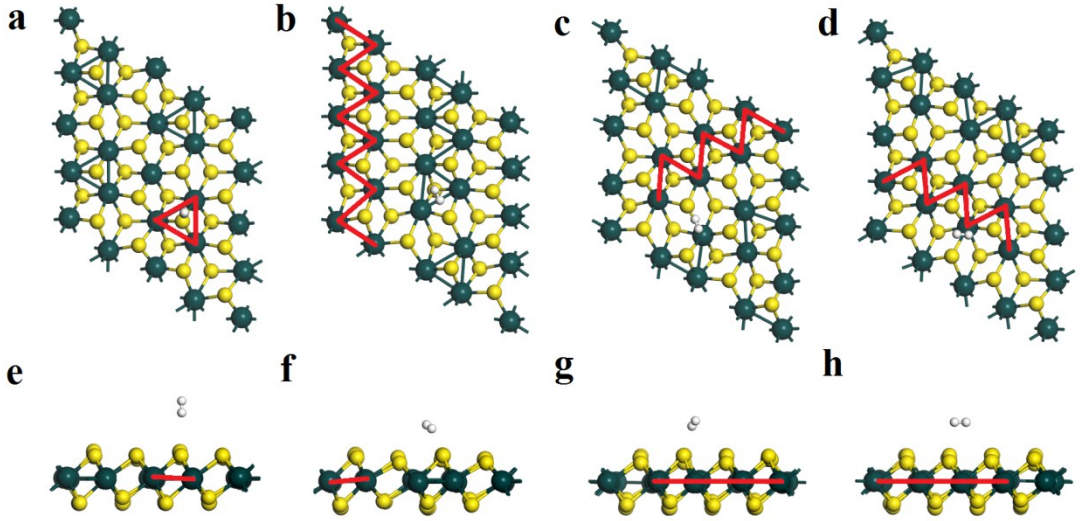

Figure S3. Geometry optimization results for single hydrogen molecule adsorbed on 1T MoS_2; (a) and (e) right above the upper layer S atom site (b) and (f) right above the lower layer S atom site (c) and (g) right above the Mo atom site (d) and (h) above the middle of Mo atom and upper layer S atom.

Figure S3 presents the other four cases when hydrogen adsorbed on the 1T-phase MoS_2, the results also show that the structure of 1T-phase MoS_2 changes in different ways when the adsorption sites are different. Except for the first one, we can see that the zipper structure appears after the geometry optimization. For the one that the hydrogen molecule was set above the upper layer S atom site, after optimization, the neighboring three Mo atoms formed bonds, constituted a triangle structure. Such structure is very similar to the 1T'' MoS_2 structure[3].

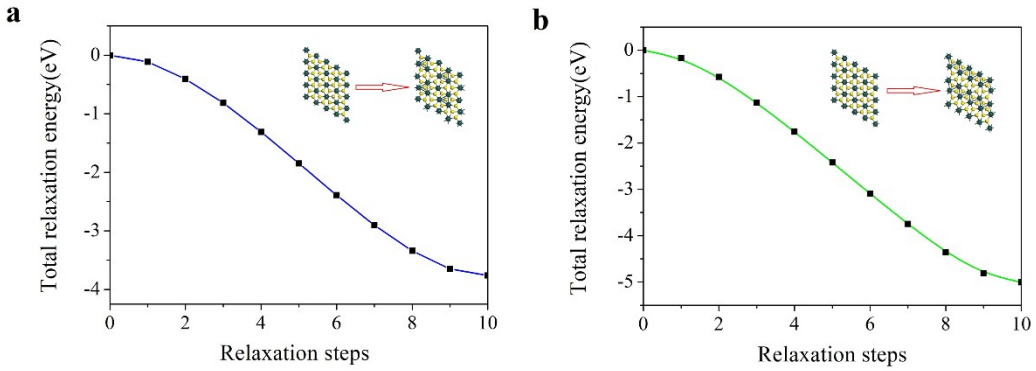

Figure S4. TS search results of two situations of one hydrogen molecule adsorbed on 1T MoS_2. (a) hydrogen molecule right above the upper layer S atom site (b) hydrogen molecule above the middle of Mo atom and lower layer S atom.

Figure S4 shows the energy change results while hydrogen molecules adsorbed on two different sites of the 1T phase MoS_2. Both of them has no energy barrier during conversion. For the first one (shown as Figure S4 (a)), the target structure is similar to that of 1T'' MoS_2, the relaxation energy is about -3.76eV. The target structure for the second one (shown as Figure S4 (b)) is 1T'-like structure, the relaxation energy is about 5.01eV.

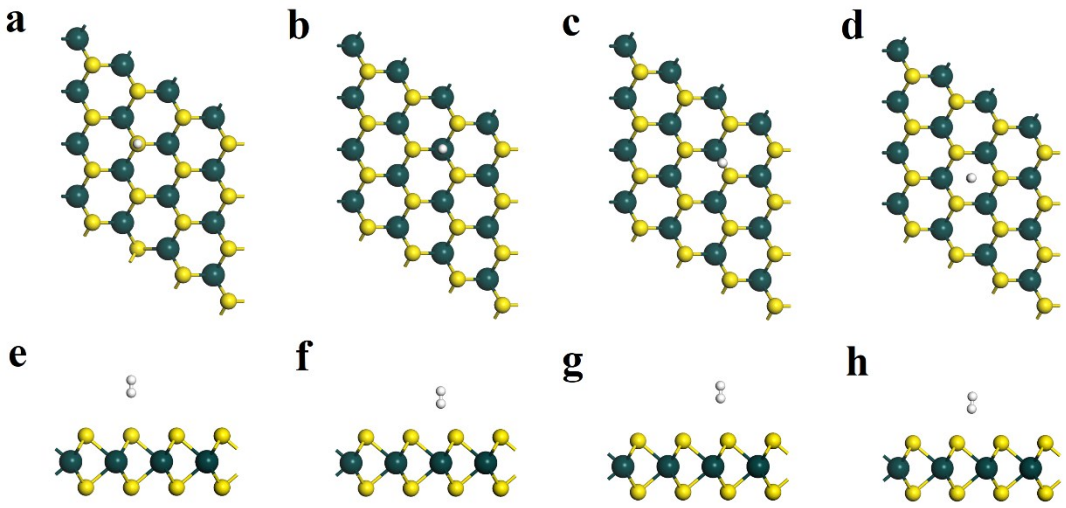

Figure S5. Positions of a hydrogen molecule adsorbed on the pristine-2H MoS_2 (a) and (e) Top of S atom (b) and (f) Top of Mo atom (c) and (g) Top of the middle of S-Mo band (d) and (h) Top of the center of hexagonal

Figure S5 shows our previous result of hydrogen molecule adsorbed on the pristine-2H MoS_2[4]. The most stable position of adsorption is shown in (b) and (f) (After comparing the results shown in Table S3). The calculated hydrogen adsorption energy is -0.188eV, which is not in the provided range (-0.2 to -0.6 eV) of the ideal adsorption energy for hydrogen storage. Indicating that the phase change really gives a promotion to the 2H MoS_2 in hydrogen storage applications.

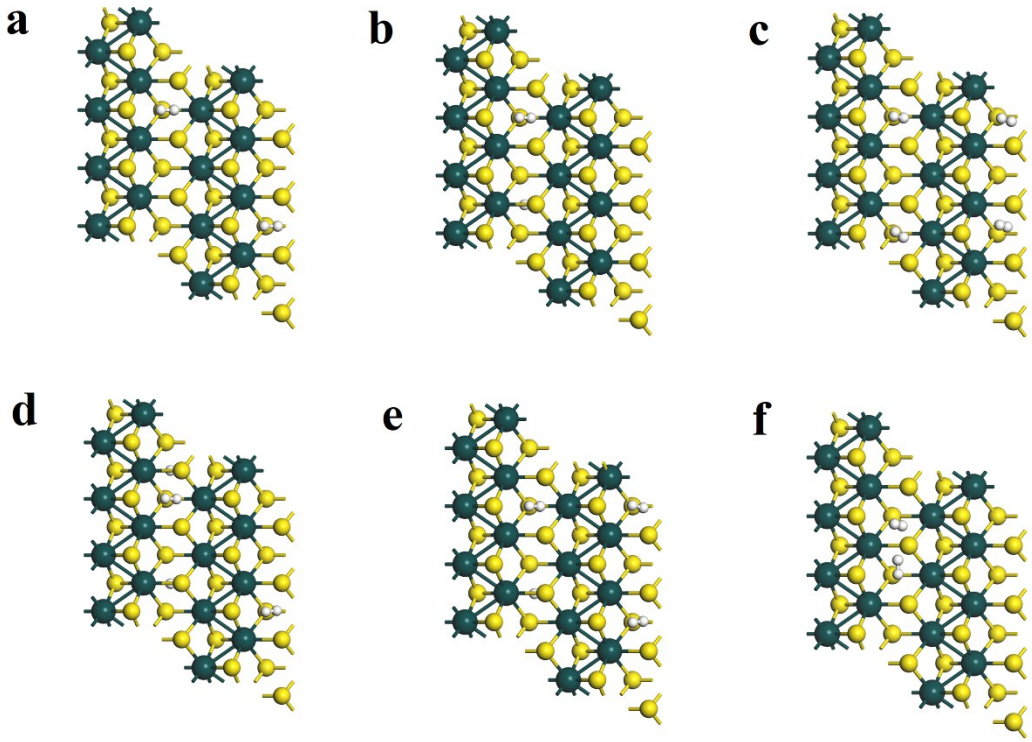

Figure S6. Geometry optimization results of 2 or 4 hydrogen molecules adsorbed with different cases of arrangement. (a) $2H_2$ on the same side (b) $2H_2$ on different sides (c) $4H_2$ on the same side (d) and (e) $4H_2$ on different sides (f) $2H_2$ on the neighbouring sites

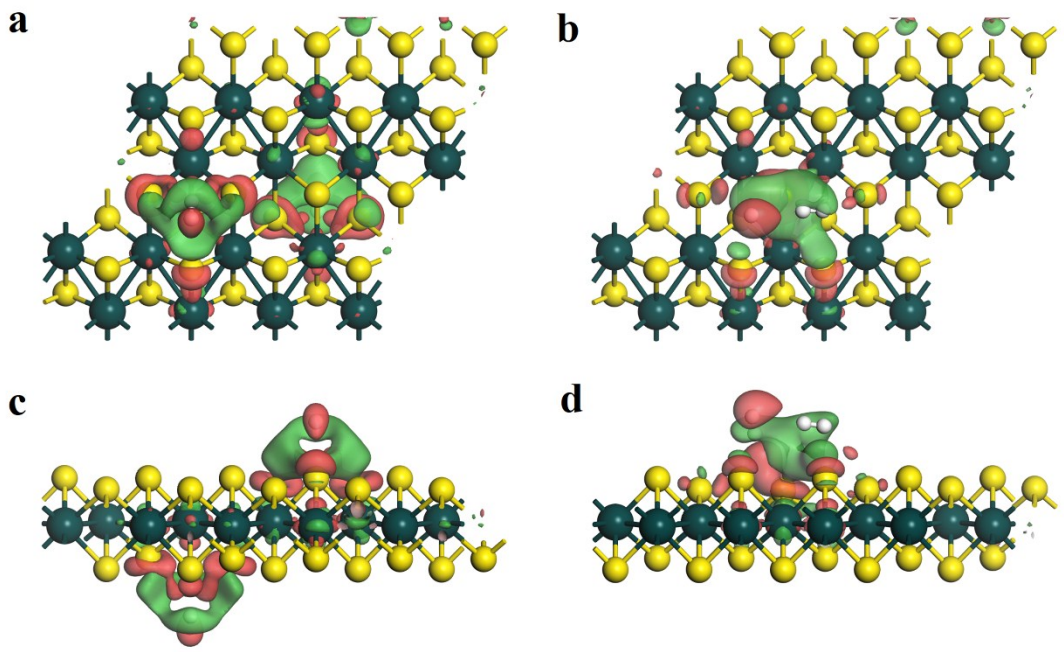

Figure S7. Electron density difference results for the cases when two hydrogen molecules adsorbed on (a) and (c) different sides of 1T' MoS_2 plane (b) and (d) neithbouring sites of 1T' MoS_2. The isosurface value is taken as 0.001 e/bohr^3.

Figure S7 shows the electron density difference results for the cases when two adsorbed hydrogen molecules arranged in different ways. The red area presents positive value area while the green area is negative area. The results show that S atoms near the adsorbed hydrogen molecules tend to obtain electrons and the atoms in a hydrogen molecule closer to the basement material plane tend to lose electrons. Moreover, from Figure S7 (b) and (d) we can also see that: when two hydrogen molecules were set close enough, they had interaction each other. And that makes their resultant force to the substrate material different from that of separated two molecules.

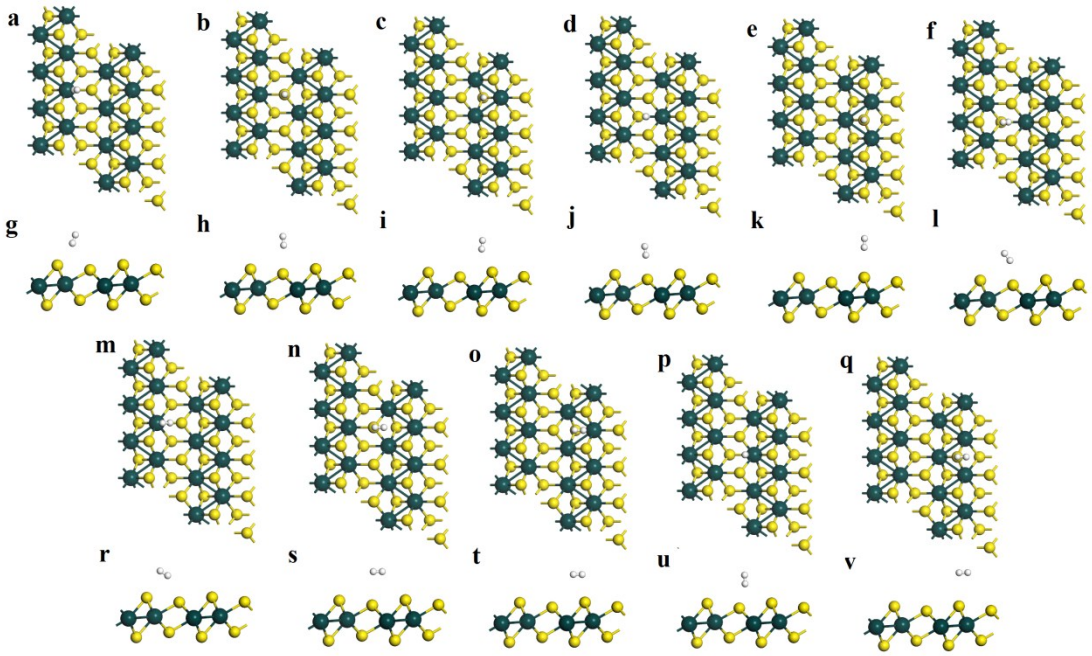

Figure S8. Geometry optimization results for single hydrogen molecule adsorbed on 1T' MoS_2; (a) and (g) edge on the Mo-1 site (b) and (h) edge on the upper S-1 site (c) and (i) edge on the lower S-2 site (d) and (j) edge on the Mo-2 site (e) and (k) edge on the upper S-2 site (f) and (l) edge on the lower S-1 site (m) and (r) side on the Mo-1 site (n) and (s) side on the upper S-1 site (o) and (t) side on the lower S-2 site (p) and (u) side on the Mo-2 site (q) and (v) side on the upper S-2 site

Figure S8 presents the other situations when a single hydrogen molecule adsorbed on the 1T' MoS_2. We can see that if the hydrogen molecule was set vertically to the plane, the optimization results of hydrogen molecules also tend to be vertically. Also for the ones set horizontally, the results were mostly horizontally(escept for the one shown in (p) and (u)). Then combined with the adsorption energy result. The adsorption system structures with higher adsorption energies usually the ones that hydrogen molecules set in the hollow sites of the 1T' MoS_2 structures(such as the ones shown in Figure S2 (c) and Figure S8 (f)). While that set in the ledge sites often have lower adsorption energy(such as the ones shown in Figure S8 (e) and (o)). That indicates hollow site can better accommodate target gas molecules. In other words, target gas molecules adsorbed on the hollow sites of the adsorbing materials can form a more stable adsorption system. Similar results has been shown in other studies[5-6].

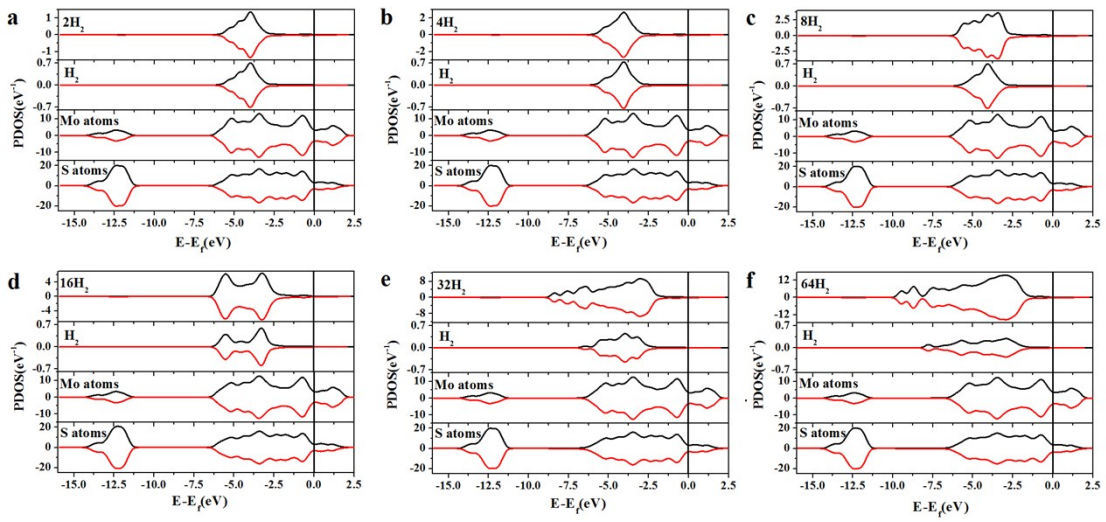

Figure S9. PDOS of H_2 adsorpton system for (a) $2H_2$ molecules (b) $4H_2$ molecules (c) $8H_2$ molecules (d) $16H_2$ molecules (e) $32H_2$ molecules (f) $64H_2$ molecules absorbed on the 1T' MoS_2

Figure S9 shows the PDOS results of multiple hydrogen molecules adsorbed on the 1T' MoS_2. With the increase of the quantity of hydrogen molecules, the PDOS for Mo atoms and S atoms hardly changed, while the PDOS for hydrogen became dispersed. And that makes the overlapping of the electron orbit between the hydrogen molecules and 1T' MoS_2. As a consequence, the average adsorption energy increases.

Table S1

Structural parameters of 1T and 1T' MoS_2 in previous studies

Number	Type(1T/1T')	Structural Parameters(Å)				reference
		l_{ca}/l_{cb}	θ	$l_{Mo\text{-}S}$	$l_{Mo\text{-}Mo}$	
1	1T	3.10/3.10	120		-	[7]
	1T'	3.11/5.63				
2	1T'	3.18/5.75				[8]
3	1T'	3.17/5.72		2.41		[9]
4	1T'	3.14/5.69	119.0			[10]
5	1T	3.16/3.16	120		-	[11]
6	1T	3.19/3.19	120	2.46	-	[12]
	1T'	3.19/5.75		2.42-2.50	2.75	
7	1T	3.16/3.16	120			[13]
	1T'	3.21/5.78				
8	1T'			2.39-2.51	2.77	[14]
9	1T	3.24/3.24	120	2.427	-	This study
	1T'	3.19/5.70	119.25	2.386-2.463	2.778	

l_{ca}/l_{cb}: lattice constants a/b;

θ: lattice angle;

$l_{Mo\text{-}S}$: length of Mo-S bond;

$l_{Mo\text{-}Mo}$: length of Mo-Mo bond

Table S2

The primitive values of $E_{hyd+sys}$, E_{sys} and E_{hyd} for single hydrogen molecule adsorption

Structures	$E_{hyd+sys}$ (Ha)	E_{sys} (Ha)	E_{hyd} (Ha)
2H MoS_2-1	-14224.4150474	-14223.2739505	-1.1359179
2H MoS_2-2	-14224.4169791		
2H MoS_2-3	-14224.4154171		
2H MoS_2-4	-14224.4164899		
1T MoS_2-1	-14224.0008995	-14222.7239255	
1T MoS_2-2	-14224.0292101		
1T MoS_2-3	-14224.0310464		
1T MoS_2-4	-14224.0307476		
1T MoS_2-5	-14224.0427778		
1T' MoS_2-1	-14224.0600580	-14222.9137439	
1T' MoS_2-2	-14224.0588839		
1T' MoS_2-3	-14224.0590833		
1T' MoS_2-4	-14224.0608980		
1T' MoS_2-5	-14224.0569484		
1T' MoS_2-6	-14224.0609222		
1T' MoS_2-7	-14224.0607833		
1T' MoS_2-8	-14224.0578881		
1T' MoS_2-9	-14224.0585278		
1T' MoS_2-10	-14224.0606484		
1T' MoS_2-11	-14224.0614859		
1T' MoS_2-12	-14224.0659431		

Table S3

The primitive values of $E_{hyd+sys}$ for multiple hydrogen molecule adsorption

Number of H_2 molecules	$E_{hyd+sys}$ for 1T'-phase MoS_2 (Ha)	**Number of H_2 molecules**	$E_{hyd+sys}$ for 1T'-phase MoS_2 (Ha)
2	-14225.2131473	**18**	-14243.6425001
3	-14226.3603560	**20**	-14245.9374215
4	-14227.5074933	**22**	-14248.2959926
5	-14228.6566158	**24**	-14250.6562953
6	-14229.8041312	**28**	-14255.3078347
7	-14230.9502832	**32**	-14259.8996812
8	-14232.1001668	**40**	-14269.2129720
10	-14234.4172001	**48**	-14278.4401752
12	-14236.7192759	**52**	-14283.1267153
14	-14239.0168379	**56**	-14287.8010567
16	-14241.3200993	**64**	-14297.1736025

Table S4

The values of total adsorption energy $E_{ads-tol}$ for single hydrogen molecule adsorption.

Structures	**2H MoS_2**	**Structures**	**1T' MoS_2**
	$E_{ads-tol}$(eV)		$E_{ads-tol}$(eV)
1T MoS_2-1	-0.1409	**1T' MoS_2-1**	-0.2829
1T MoS_2-2	-0.1884	**1T' MoS_2-2**	-0.2509
1T MoS_2-3	-0.1510	**1T' MoS_2-3**	-0.2564
1T MoS_2-4	-0.1802	**1T' MoS_2-4**	-0.3058
		1T' MoS_2-5	-0.1983
Structures	**1T MoS_2**	**1T' MoS_2-6**	-0.3064
	$E_{ads-tol}$(eV)	**1T' MoS_2-7**	-0.3026
1T MoS_2-1	-3.861	**1T' MoS_2-8**	-0.2238
1T MoS_2-2	-4.631	**1T' MoS_2-9**	-0.2413
1T MoS_2-3	-4.681	**1T' MoS_2-10**	-0.2990
1T MoS_2-4	-4.673	**1T' MoS_2-11**	-0.3218
1T MoS_2-5	-5.001	**1T' MoS_2-12**	-0.4430

Table S5

The absolute values of average adsorption enregy $E_{ads\text{-}ave}$ of hydrogen molecules for different arrangement cases.

Number of H_2 molecules	1T' MoS_2		Number of H_2 molecules	1T' MoS_2	
	N_1/N_2	$E_{ads\text{-}ave}$(eV)		N_1/N_2	$E_{ads\text{-}ave}$(eV)
2	2/0	0.3765	**4**	4/0	0.3416
	1/1	0.3751		3/1	0.3412
	2n/0	0.4351		2/2	0.3407

N_1, N_2: Number of hydrogen molecules on the two sides of 1T' MoS_2 plane.

2n means two molecules on the neighbouring sites.

Table S6

The absolute values of total adsorption energy $E_{ads\text{-}tol}$ and average adsorption energy $E_{ads\text{-}ave}$ for multiple hydrogen molecuels adsorption.

Number of H_2 molecules	1T' MoS_2		Number of H_2 molecules	1T' MoS_2	
	$E_{ads\text{-}tol}$(eV)	$E_{ads\text{-}ave}$(eV)		$E_{ads\text{-}tol}$(eV)	$E_{ads\text{-}ave}$(eV)
1	0.443	0.443	**16**	6.304	0.394
2	0.7502	0.3751	**18**	7.68	0.4267
3	1.184	0.3947	**20**	8.3626	0.4181
4	1.3627	0.3407	**22**	10.6684	0.4849
5	1.722	0.3444	**24**	13.0757	0.5448
6	2.0376	0.3396	**28**	16.0109	0.5718
7	2.3161	0.3309	**32**	17.3218	0.5413
8	2.6961	0.337	**40**	23.4702	0.5868
10	3.926	0.3926	**48**	27.2759	0.5682
12	4.7489	0.3957	**56**	34.7193	0.62
14	5.4489	0.3892	**64**	42.4801	0.6637

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diffusion ontwo-dimensional Ti_2C monolayer, International Journal of Hydrogen Energy, 2017, 42, 27214-27219.

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