Supplementary information

Tuning the Phase Stability and Surface HER Activity of 1T′-MoS_2 by Covalent Chemical Functionalization

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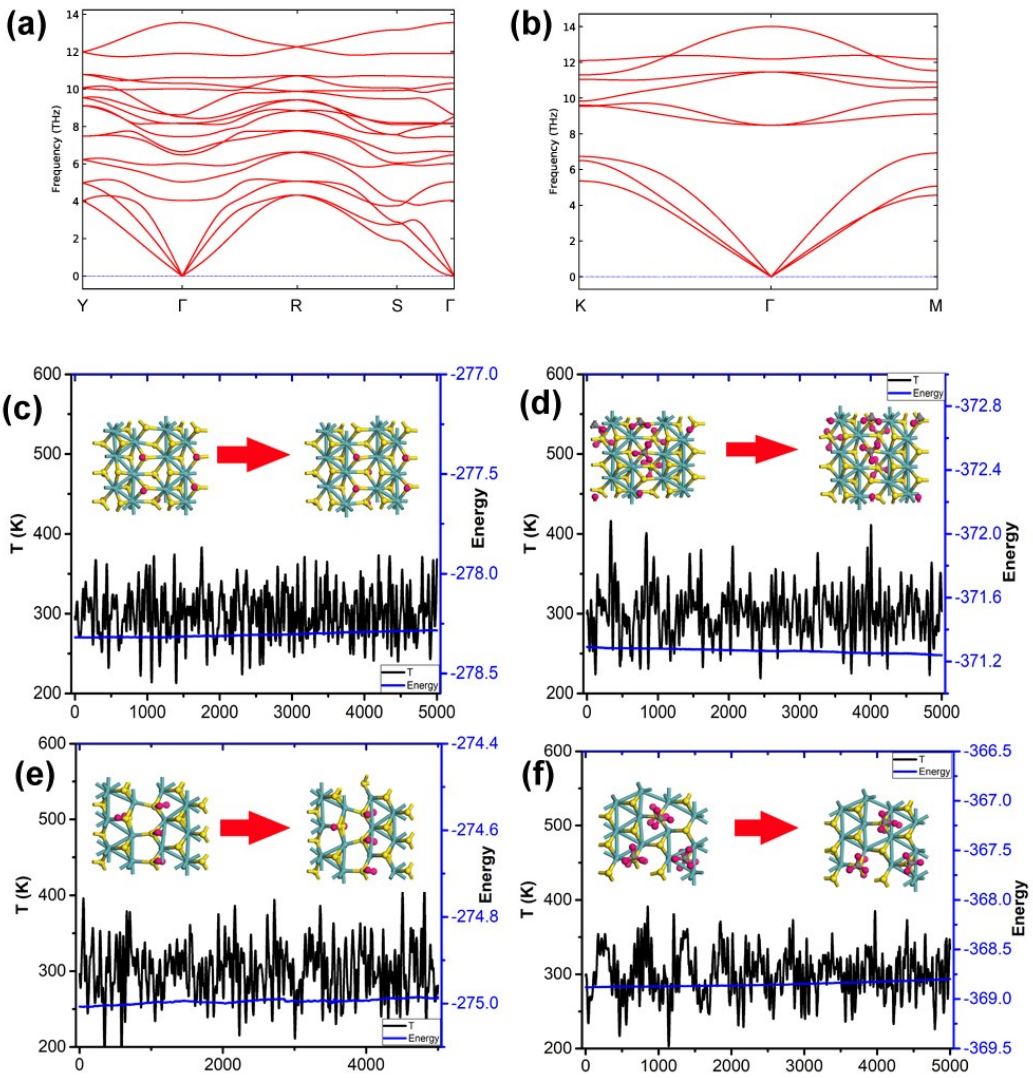
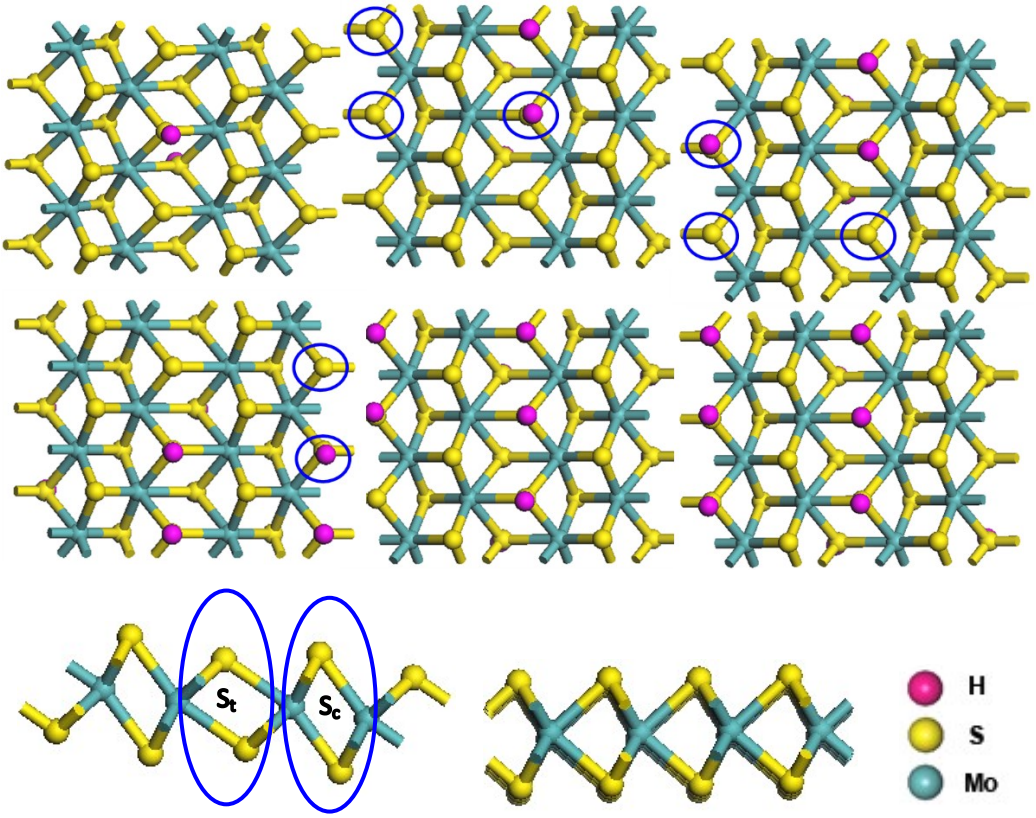


Figure S1. The calculated phonon spectra of the pristine 1T′-MoS_2 (a) and 2H-MoS_2 (b). The AIMD simulations of 1T -MoS_2 with -H (33.3 %, (c)) and –CH_3 (25 %, (d)), 2H-MoS_2 with H (33.3 %, (e)) and –CH_3 (25 %, (f)), the temperature and potential energy curve as the function of time under 300K with a time step of 1 fs.

Table S1. The electronic energy of all the studied structures with and without dipole-correction along the z direction (the * indicates the results for dipole correction). θ is the coverage concentration of various functional groups.

Phase	functionalized 1T′				functionalized 2H			
θ (%)	8.3	16.7	25.0	33.3	8.3	16.7	25.0	33.3
-H	-262.24	-268.97	-276.14	-282.49	265.85	-270.30	-276.75	-280.98

-H*	-262.18	-268.90	-276.14	-282.40	-265.42	-270.31	-276.76	-281.00
-CH_3	-295.59	-335.69	-376.08	-415.62	-295.56	-336.11	-372.50	-409.79
-CH_3*	-295.58	-335.59	-376.11	-415.54	-295.57	-336.12	-372.47	-409.58
-CH_2CH_2OH	-340.95	-426.47	-512.29	-597.44	-344.70	-427.37	-508.71	-592.16
-CH_2CH_2OH*	-340.99	-426.28	-511.88	-597.30	-344.68	-427.32	-508.71	-591.91
-CH_2CONH_2	-351.10	-447.29	-543.64	-638.22	-354.99	-444.96	-537.64	-628.21
-CH_2CONH_2*	-351.16	-447.30	-543.65	-638.18	-355.04	-444.96	-537.64	-628.21
-CH_2COOH	-340.32	-424.87	-510.45	-594.47	-344.19	-423.66	-504.22	-584.41
-CH_2COOH*	-340.31	-424.91	-510.46	-594.52	-344.19	-423.66	-504.22	-584.41
-NH_2Ph	-423.61	-590.87	-759.17	925.84	-427.25	-592.40	-756.46	-921.95
-NH_2Ph*	-423.61	-590.82	-759.09	-925.69	427.24	-592.36	-756.38	-921.83
-NO_2Ph	-429.73	-603.12	-777.50	950.38	-433.44	-604.86	-774.99	-946.65
-NO_2Ph*	-429.00	-601.03	-777.50	-950.38	-433.05	-604.06	-773.16	-946.65



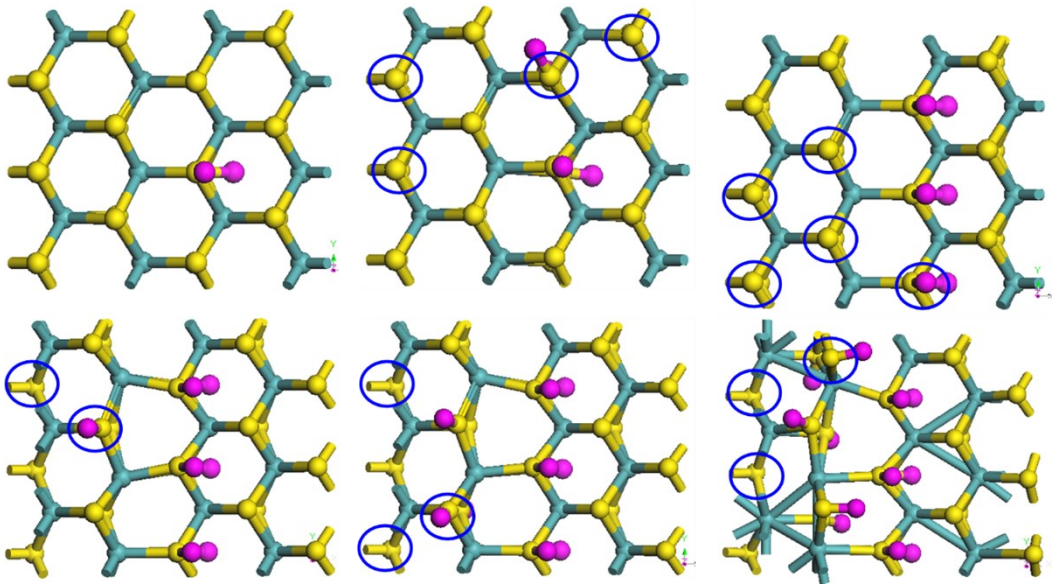


Figure S2. a) All the possible hydrogen adsorption sites are examined (the possible sites is marked with the blue circle and the blue circle with hydrogen is the stable adsorption site of hydrogen on 1T′-MoS_2 and 2H-MoS_2 monolayer), b) S_t more close to the Mo layer is more active for hydrogen adsorption and S_c is relatively inert.

Table S2. The optimal lattice parameters of 1T′-MoS_2 and 2H-MoS_2 monolayer functionalized by different functional groups at the coverage ranging from 8.3% to 33.3%.

Functional groups	Coverage (%)	a(Å)	b(Å)
-Ph-NH_2	8.3	11.498	9.638
	16.7	11.600	9.779
	25.0	11.748	9.809
	33.3	11.893	9.837
-Ph-NO_2	8.3	11.479	9.604
	16.7	11.551	9.750
	25.0	11.676	9.716
	33.3	11.830	9.731
-CH_2CH_2OH	8.3	11.494	9.608
	16.7	11.544	9.761
	25.0	11.606	9.600
	33.3	11.737	9.900
-CH_3	8.3	11.512	9.620
	16.7	11.508	9.642
	25.0	11.701	9.800
	33.3	11.737	9.900
-CH_2COOH	8.3	11.494	9.611
	16.7	11.533	9.742

	25.0	11.630	9.765
	33.3	11.683	9.805
$-CH_2CONH_2$	8.3	11.497	9.606
	16.7	11.521	9.752
	25.0	11.640	9.757
	33.3	11.653	9.820
-H	8.3	11.505	9.685
	16.7	11.591	9.743
	25.0	11.730	9.811
	33.3	11.800	9.871

Table S3. Total energy (eV) of hydrogenated MoS_2 monolayer at the coverage varying from 0 to 50%. $\Delta E = E_{2H+H} - E_{1T+H}$, per unit, ΔE is the energy of per MoS_2 unit.

Coverage(%)	0	8.3	16.7	25	33.3	41.7	50
E_{1T+H} (eV)	-255.24	-262.18	-268.90	-276.14	-282.40	-288.42	-294.21
E_{2H+H} (eV)	-261.83	-265.42	-270.31	-276.76	-281.00	-283.88	-290.61
ΔE (eV)	-6.59	-3.24	-1.41	-0.62	1.40	4.54	3.60
Per unit ΔE (eV)	-0.55	-0.27	-0.12	-0.05	0.12	0.38	0.30

Table S4. The electronic energy of the 1T′-MoS_2 functionalized with $–CH_3$, $-CH_2CH_2OH$, $-CH_2CONH_2$, $-NO_2Ph$, and $-NH_2Ph$ at different S sites with the coverage spanning from 8.3% to 25 or 33.3%.

	Coverage (%)	Energy (eV, St site)	Energy (eV, Sc site)
$-CH_3$	8.3	-295.58	-268.39
	16.7	-335.59	-324.21
	25.0	-376.11	-374.46
	33.3	-415.54	-411.76
$-CH_2CH_2OH$	8.3	-341.02	-335.11
	16.7	-427.27	-415.67

	25.0	-512.19	-494.18
$-CH_2CONH_2$	8.3	-351.16	-341.73
	16.7	-447.30	-430.32
	25.0	-543.65	-516.09
$-NO_2Ph$	8.3	-429.03	-416.21
	16.7	-604.61	-576.90
	25.0	-777.52	-743.60
$-NH_2Ph$	8.3	-423.64	-421.65
	16.7	-592.06	-587.89
	25.0	-759.09	-721.14

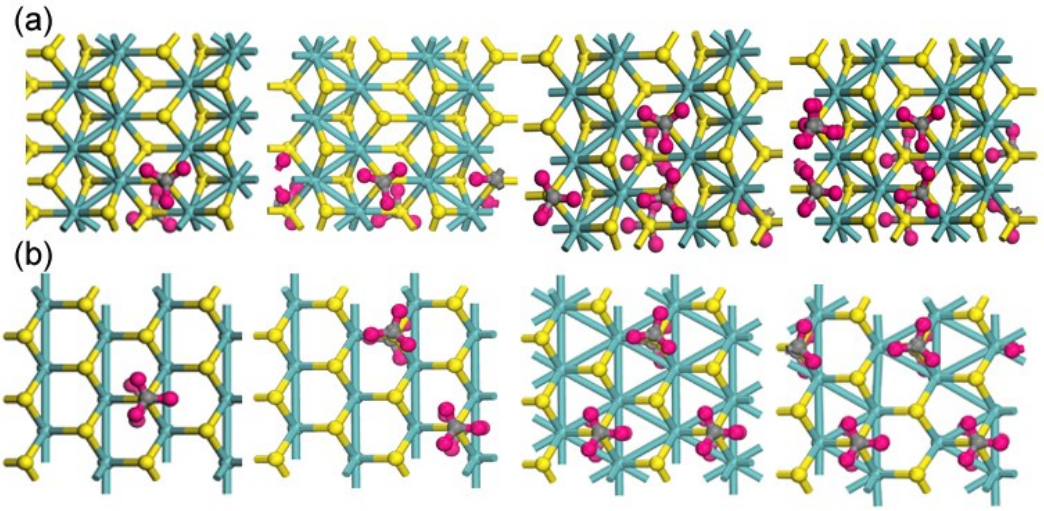


Figure S3. The most stable configurations of CH_3-functionalized 1T′-MoS_2 (a) and 2H-MoS_2 (b) as a function of different -CH_3 coverage via double-site adsorption.

Table S5. The ΔE (ΔE(eV) = E_{2H}-$E_{1T'}$, per MoS_2 unit) of 1T′-MoS_2 functionalized with different C-functional groups.

	8.3%	16.7%	25.0%	33.3%
$-CH_3$	-0.29	0.03	0.23	0.50
$-NH_2Ph$	-0.30	-0.03	0.12	0.32
$-CH_2CH_2OH$	-0.31	0.00	0.09	0.45
$-CH_2CONH_2$	-0.32	-0.12	0.09	0.81
$-CH_2COOH$	-0.32	0.10	0.52	0.85
$-NO_2Ph$	-0.34	0.00	0.01	0.31

Table S6. The change of Gibbs free energy on the reaction of functionalized 1T′-MoS_2 monolayer toward HER reaction.

functional groups	active sites	change of Gibbs energy(ΔG/eV)
pure 1T′-MoS_2		0.16
-H	1	0.67
-CH_3	1	0.58
	2	0.37
	3	0.44
-CH_2CH_3OH	1	0.34
	2	0.19
	3	0.05
-NH_2Ph	1	0.64
	2	0.59
	3	0.59
-NO_2Ph	1	0.39
	2	0.59
	3	0.46
-CH_2COOH	1	0.42
	2	0.42
	3	0.03
-CH_2CONH_2	1	0.44
	2	0.34
	3	0.71

Table S7. The band gap, the HP value, and the ΔG_H at different surface sites of functionalized 1T′-MoS_2.

	band gap (eV)	HP	ΔG (25.0 % coverage) site 1	site 2	site 3
-H	0.53	0.00	0.67 (coverage, 33.3%)		
-CH_3	metallic	-0.17	0.58	0.37	0.44
-NH_2Ph	0.17	-0.30	0.64	0.59	0.59
-CH_2CH_2OH	metallic	-0.15	0.35	0.19	0.05
-CH_2CONH_2	0.01	0.07	0.44	0.34	0.70
-CH_2COOH	metallic	0.05	0.42	0.43	0.03

-NO_2Ph	metallic	0.26	0.40	0.59	0.46