Supporting Information

Tuning the Activity of the Inert MoS_2 Surface via Graphene Oxides Support Doping towards the Chemical Functionalization and Hydrogen Evolution: A Density Functional Study

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Table S1: The binding energy (E_b) and diffusion energy barrier (TS) (in eV) for H adsorption on MoS_2/graphene and GOs with 0.32 epoxy concentration by DMOL3 and VASP.

structure	**DMOL3**			**VASP**		
	E_b		TS	E_b		TS
	PBE-D2	PBE-D2[a]		PBE-D2	PBE-D3	
MoS_2/Graphene	0.45	0.5	0.48	0.49	0.51	0.43
MoS_2/GO	0.8	0.84	0.22	0.75	0.77	0.24

[a] E_b with the dipole correction.

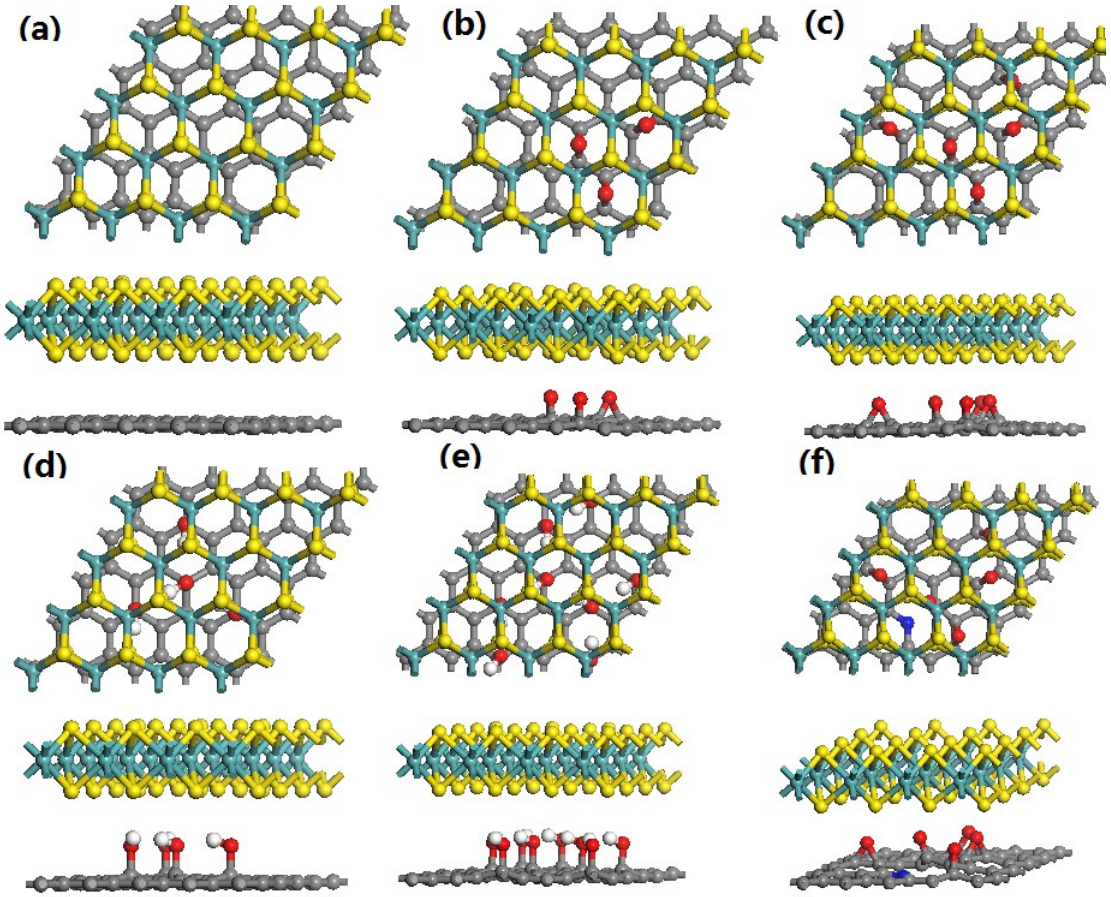

Figure S1. Top and side view of the geometrical structures of 2H-MoS_2 supported on graphene and GOs with different the epoxy and hydroxyl group concentrations and N doping.

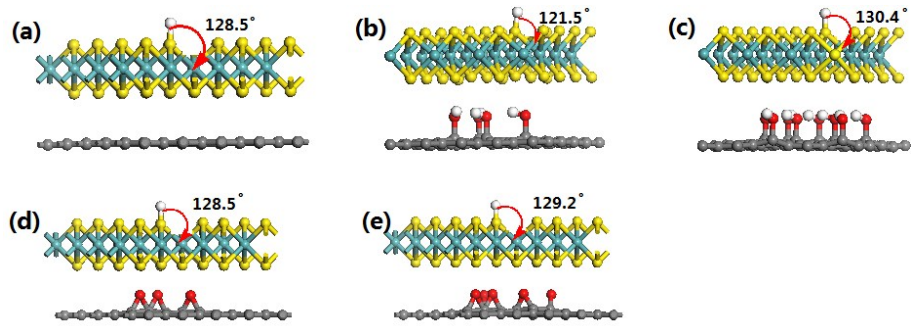

Figure S2. Comparison of the geometrical structures of H-adsorbed on MoS_2 supported on different support. The red arrows shows the bond angle θ of of H—S—Mo. Some S atoms are omitted.

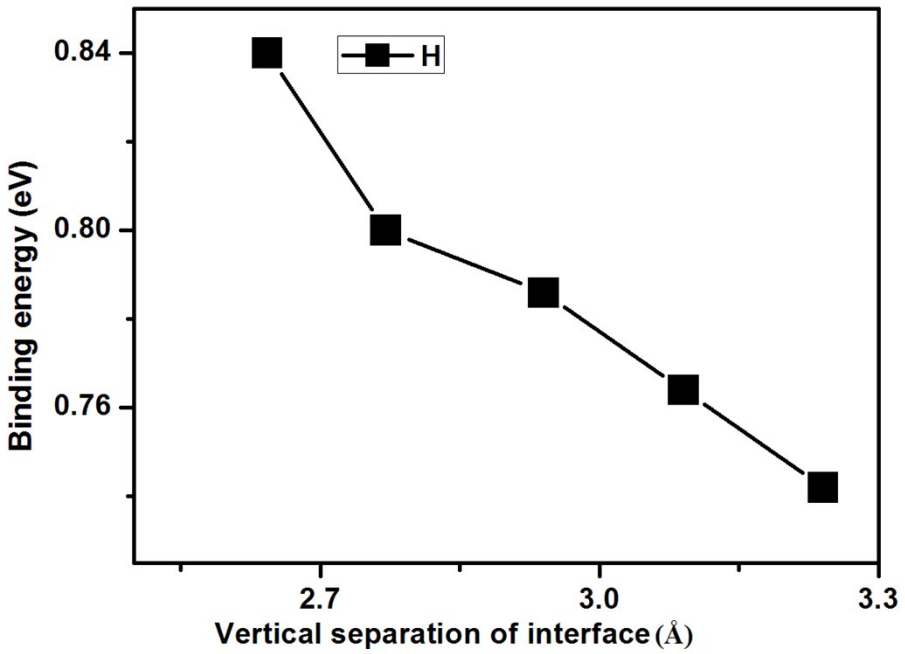

Figure S3. The binding energy for H adsorption on MoS_2/GOs with 0.32 epoxy concentration as a function of the vertical separation of interface.

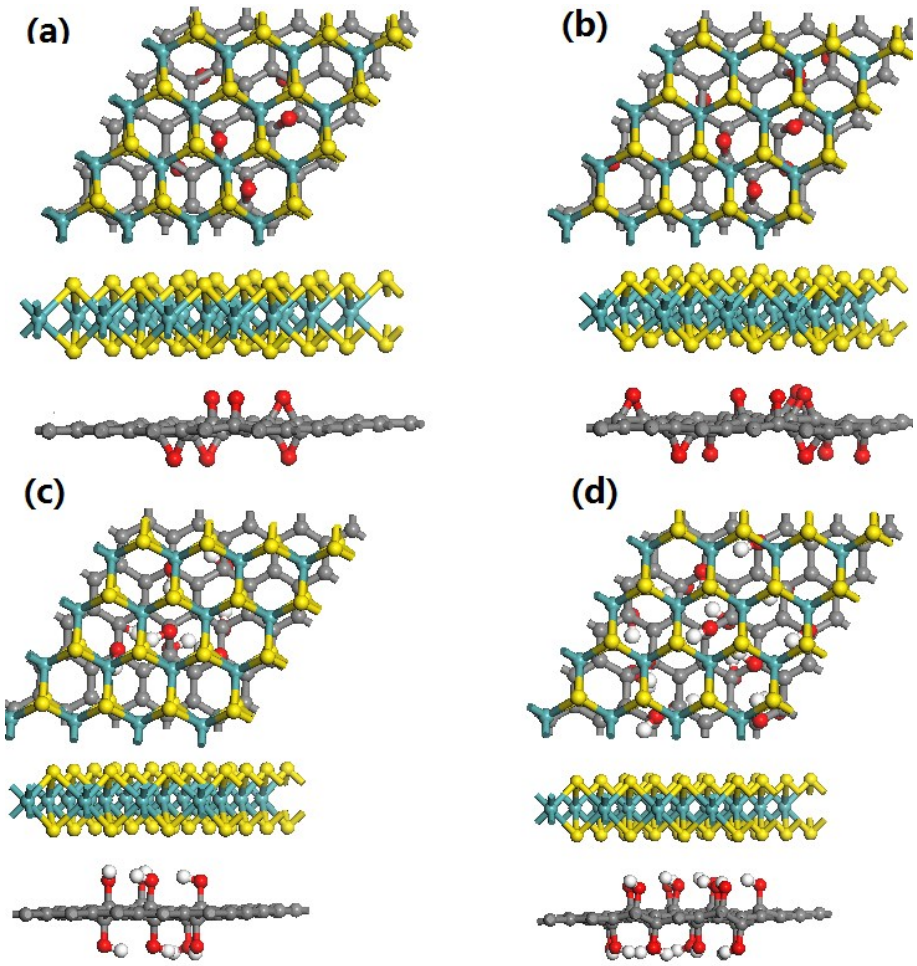

Figure S4. Top and side view of the geometrical structures of 2H-MoS_2 supported on two-side GOs with (a, b) the epoxy and (c, d) hydroxyl groups. The number of oxygen groups at each side are same. (a)-(d) 0.24, 0.4, 0.16, and 0.32 O concentrations, respectively.

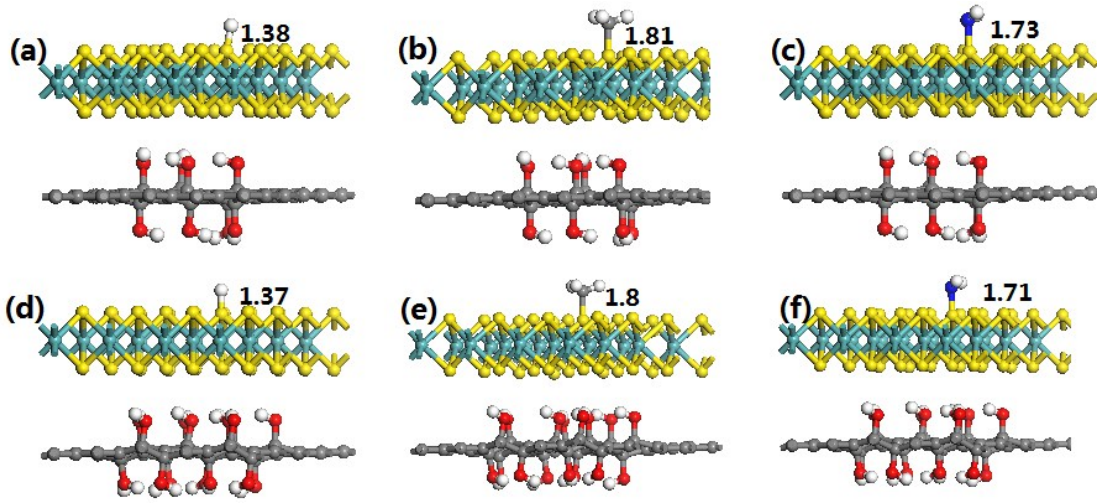

Figure S5. The geometrical structures (distance in Å) for adsorption of H, CH_3, and NH_2 on 2H-MoS_2/GOs with the hydroxyl groups.

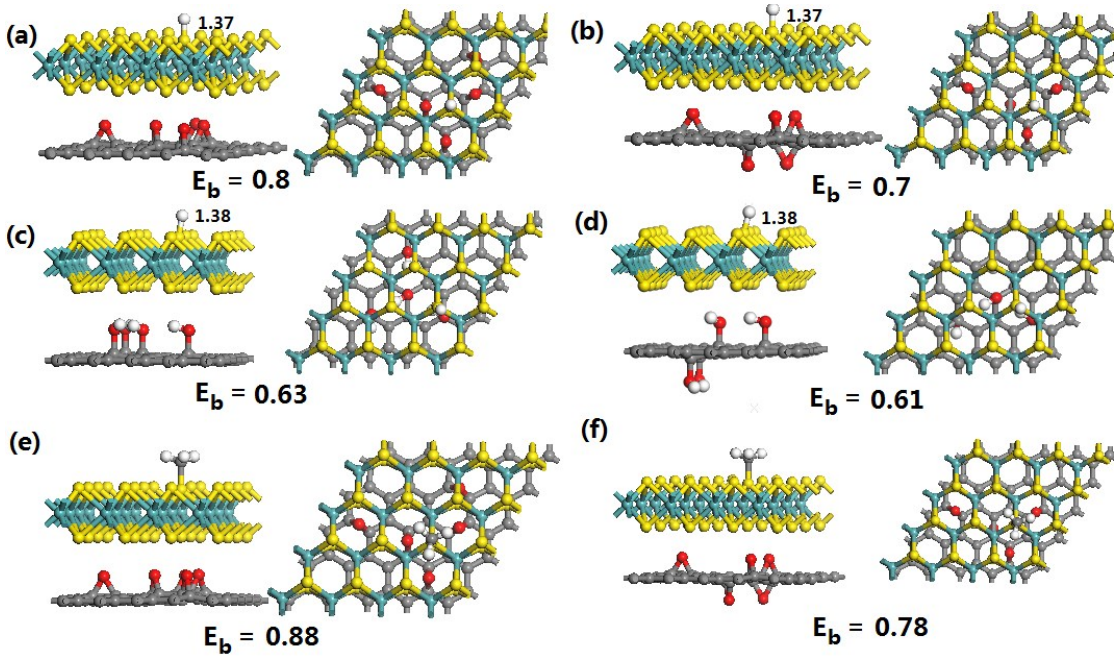

Figure S6. Top and side view of the geometrical structures for H and CH_3 adsorbed on MoS_2/GOs and the corresponding binding energy (eV): oxygen groups (a, c, and e) located at the same side and (b, d, and f) at both side.

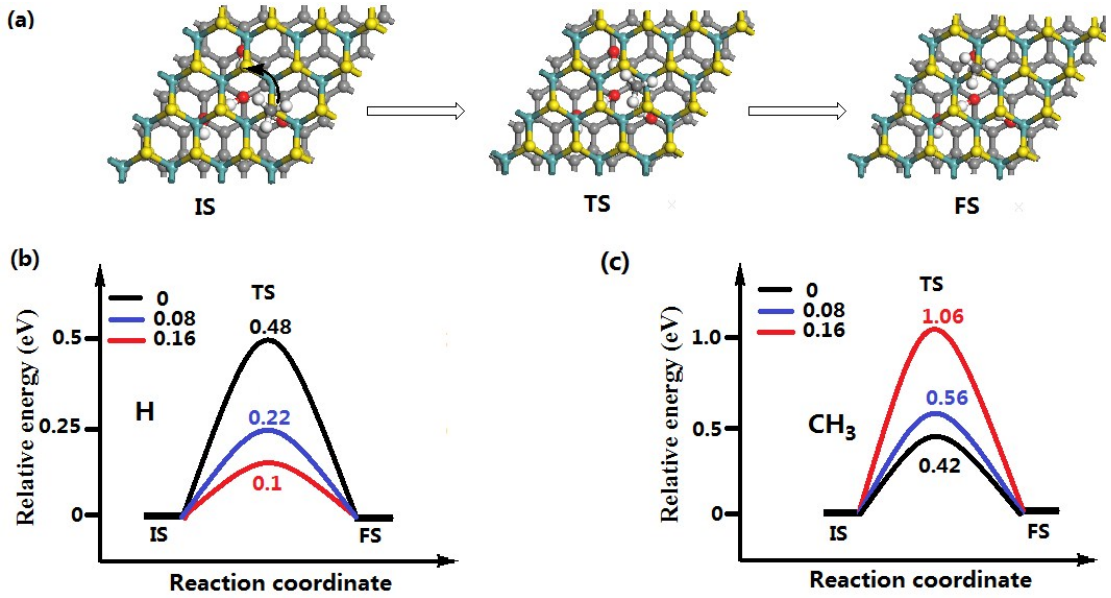

Figure S7. (a) The geometrical structures of the initial, transition, and final states for diffusion of H atom on MoS_2/GOs with 0.08 ratio of the hydroxyl to carbon. It notes that the black arrow marks the diffusion path of H from the adsorption S site to neighboring S. The relative energy paths for diffusion of adsorbed (b) H and (c) CH_3 on MoS_2/GOs with the different hydroxyl group concentration.

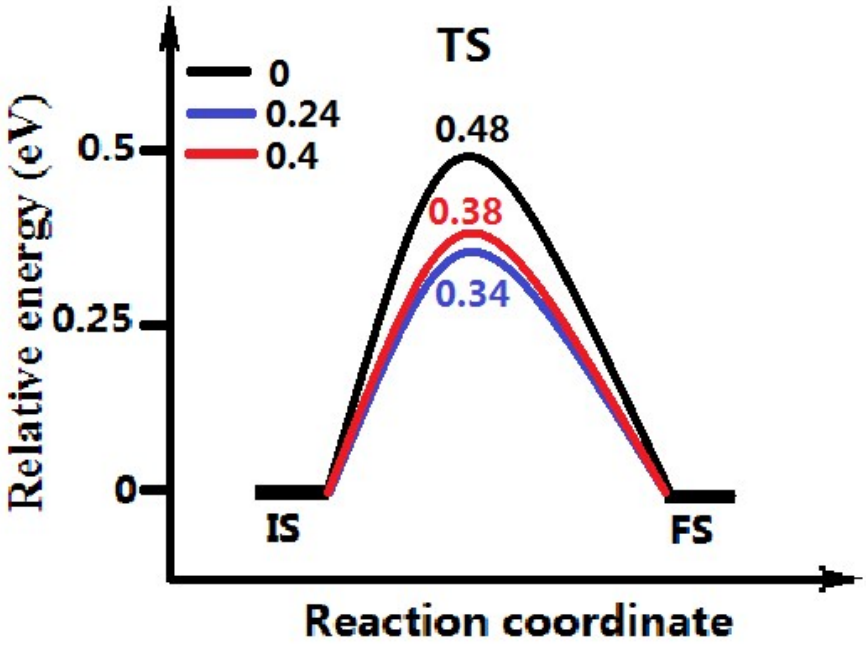

Figure S8. The relative energy paths for diffusion of adsorbed H on MoS_2/GOs with two-side epoxy groups.

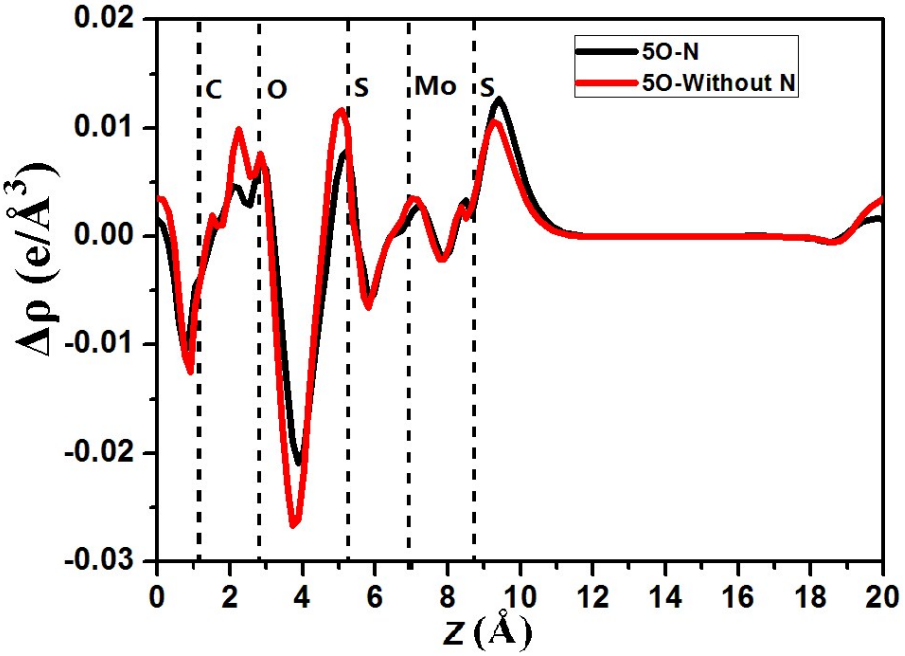

Figure S9. The profile of the planar averaged charge density difference for the MoS_2/GOs hybrids with and without N doping as a function of position in the *z*-direction. The vertical dashed lines denote the central location of each atomic layer of the MoS_2 and GOs.

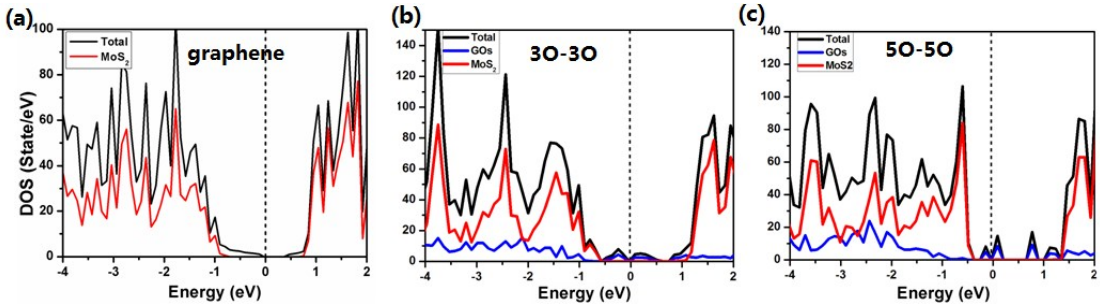

Figure S10. Total DOS and projected DOS (PDOS) of MoS_2/graphene and two-side GOs: (a) graphene and (b, c) GOs with 0.24 and 0.4 epoxy concentrations, respectively. The Fermi level is set to 0.

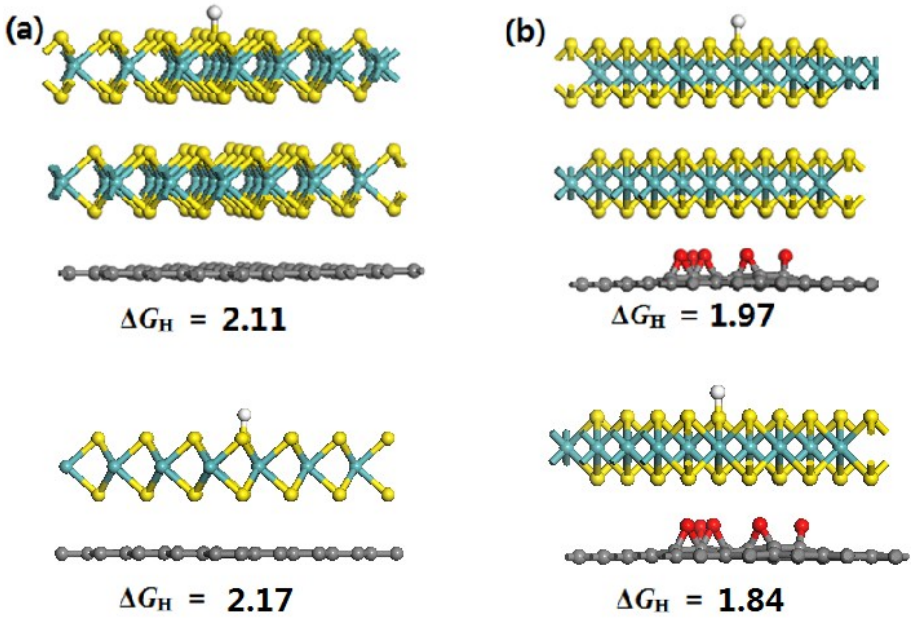

Figure S11. The geometrical structures of (a) monolayer and (b) bilayer MoS_2 supported on graphene and GOs with 0.32 ratio of O to C for H adsorption and the corresponding ΔG_H (in eV).

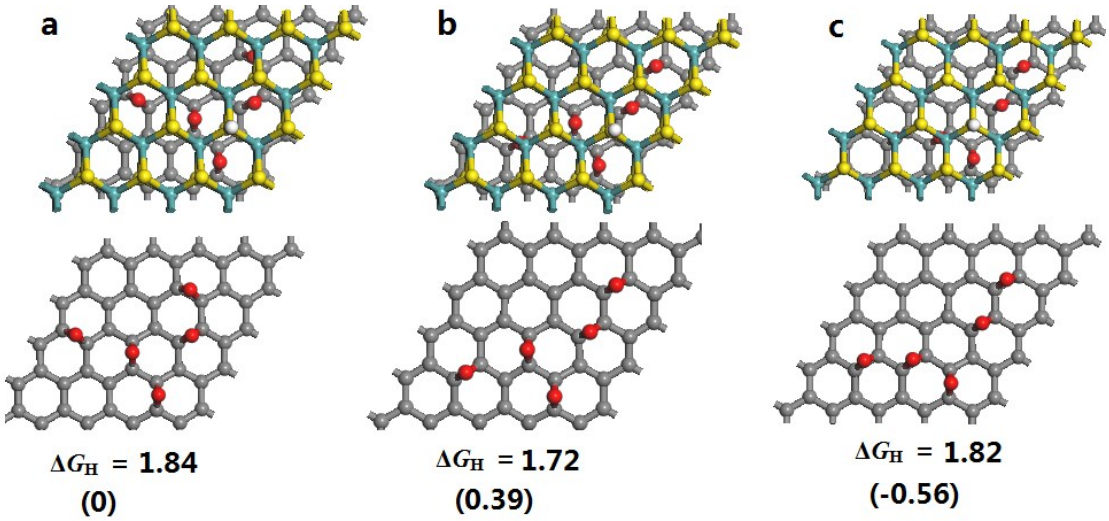

Figure S12. The geometrical structures of three MoS_2/GOs heterostructures (top panel) and GOs support (bottom panel) with fixed epoxy content. The corresponding ΔG_H (in eV) of S site and relative energies (in bracket) (in eV) of heterostructures with respect to the structure in (a).

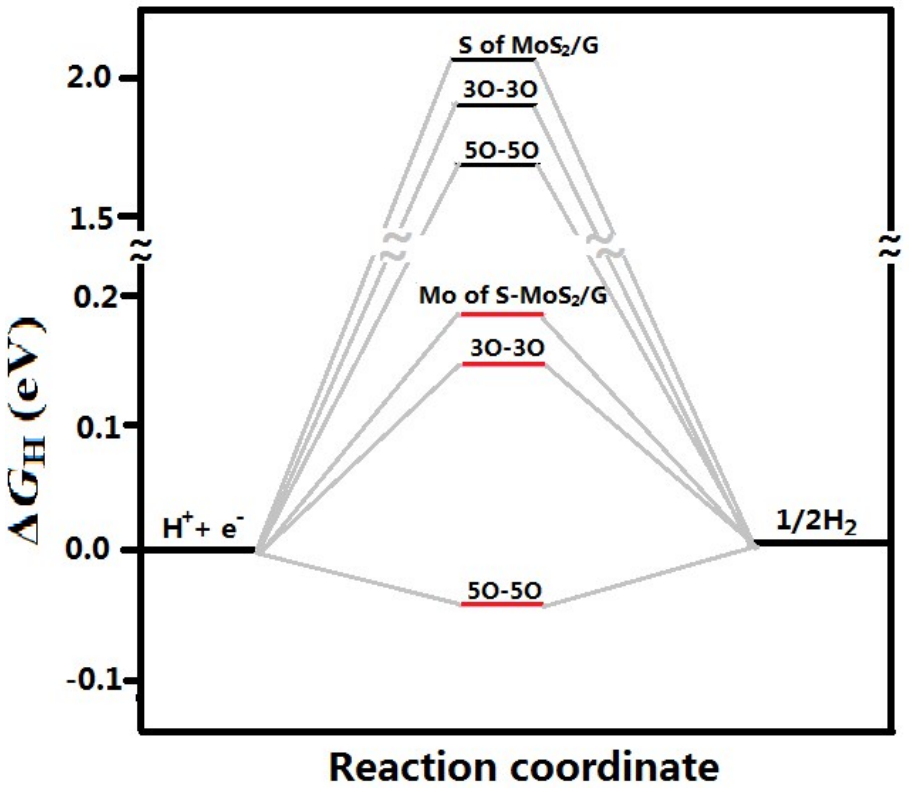

Figure S13. HER free-energy diagram for the S site (black line) of MoS_2 monolayer and exposed Mo site (red line) of S-MoS_2 supported on GOs with two-side epoxy groups (namely **m**O-mO, where the **m** represents the number of oxygen functional group at each side of graphene)

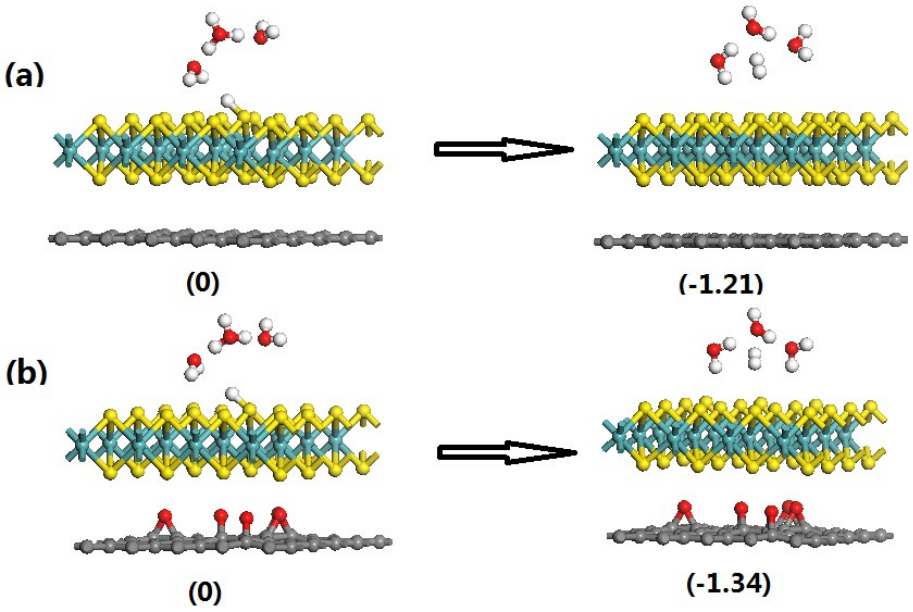

Figure S14. The geometrical structures and relative energy (in eV) for H_2 production on MoS_2 supported on (a) graphene and (b) GOs from Heyrovsky mechanism.

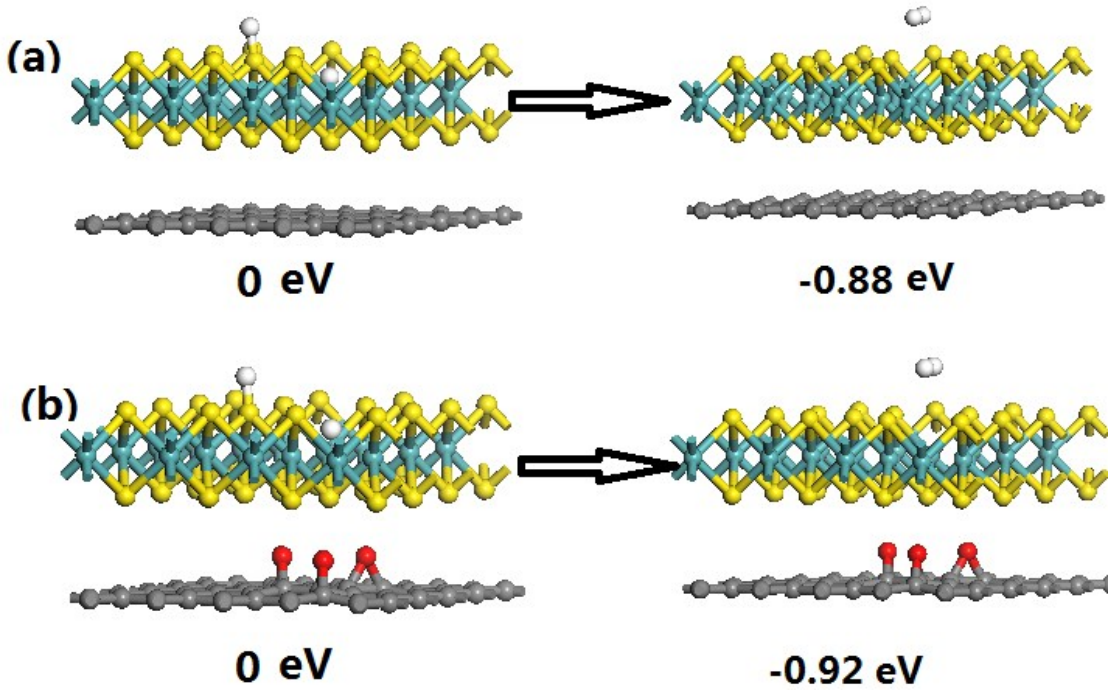

Figure S15. The geometrical structures for H_2 formation process on S-MoS_2 supported on (a) graphene and (b) GOs through Tafel mechanism and the relative energy.

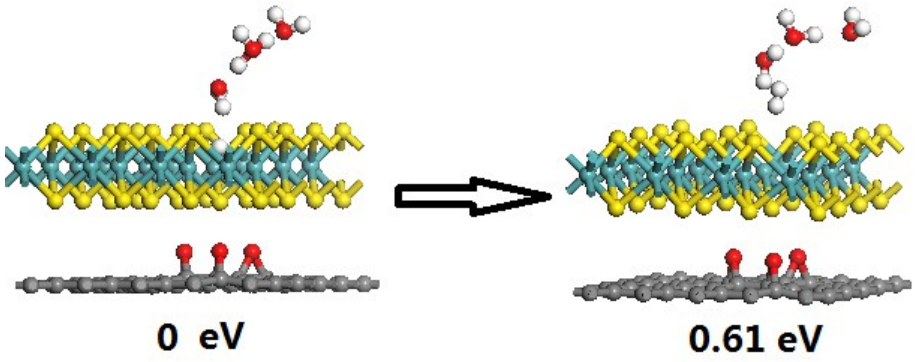

Figure S16. The geometrical structures and relative energy (in eV) for H_2 production on S-MoS_2/GOs through Heyrovsky mechanism.

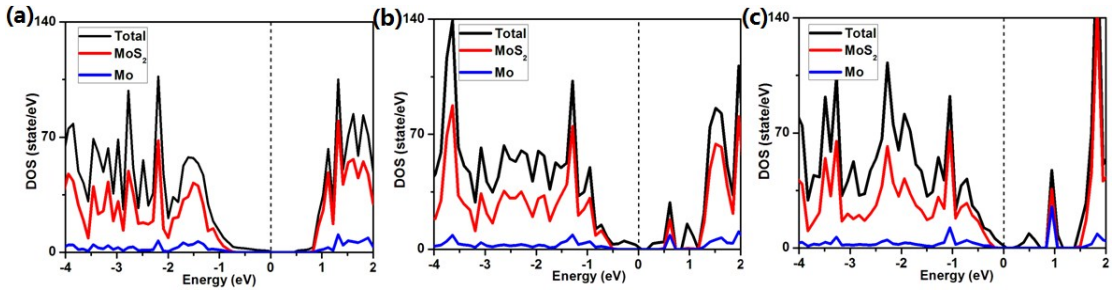

Figure S17. Total DOS and projected DOS (PDOS) of MoS_2 and the exposed Mo atoms for S-MoS_2 supported on (a) graphene and (b, c) GOs with (b) 0.12 and (c) 0.2 epoxy concentrations. The Fermi level is set to 0.