Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Theoretical Investigation on Hydrogen Evolution Reaction Mechanism at MoS_2 Heterostructure: The Essential Role of 1T/2H Phase Interface

Tian Zhang[a,†], Houyu Zhu[a,†], Chen Guo[b], Shoufu Cao[a], Chi-Man Lawrence Wu[b*], Zhaojie Wang[a], Xiaoqing Lu[a*]

[a]School of Materials Science and Engineering, China University of Petroleum, Qingdao, Shandong 266580, P. R. China

[b]Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR, P. R. China

*Corresponding authors: Chi-Man Lawrence Wu, Xiaoqing Lu

E-mail address: lawrence.wu@cityu.edu.hk, luxq@upc.edu.cn

[†]These authors have made an equal contribution to this work.

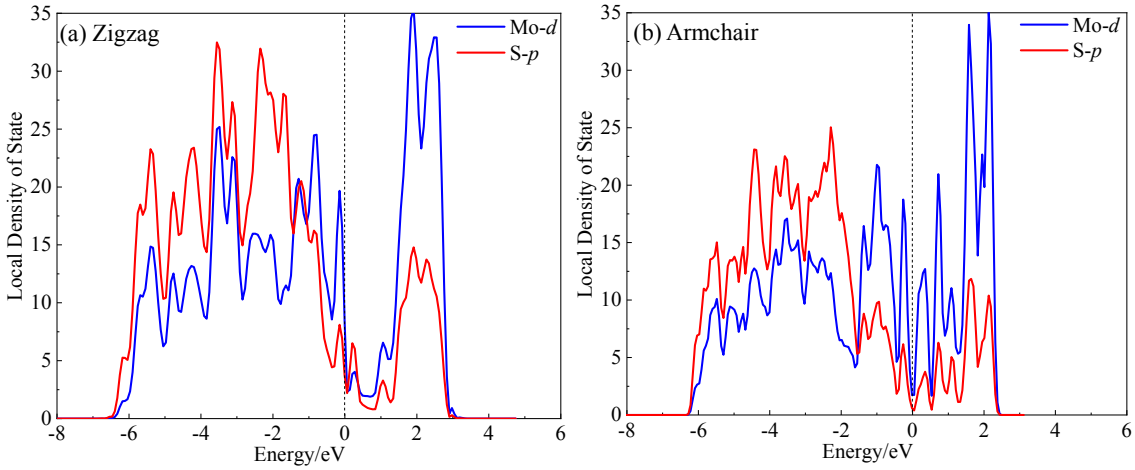

Figure S1. Density of states for the "Zigzag" (a) and "Armchair" (b) interfaces, projected on the *d*-orbitals of Mo and *p*-orbitals of S.

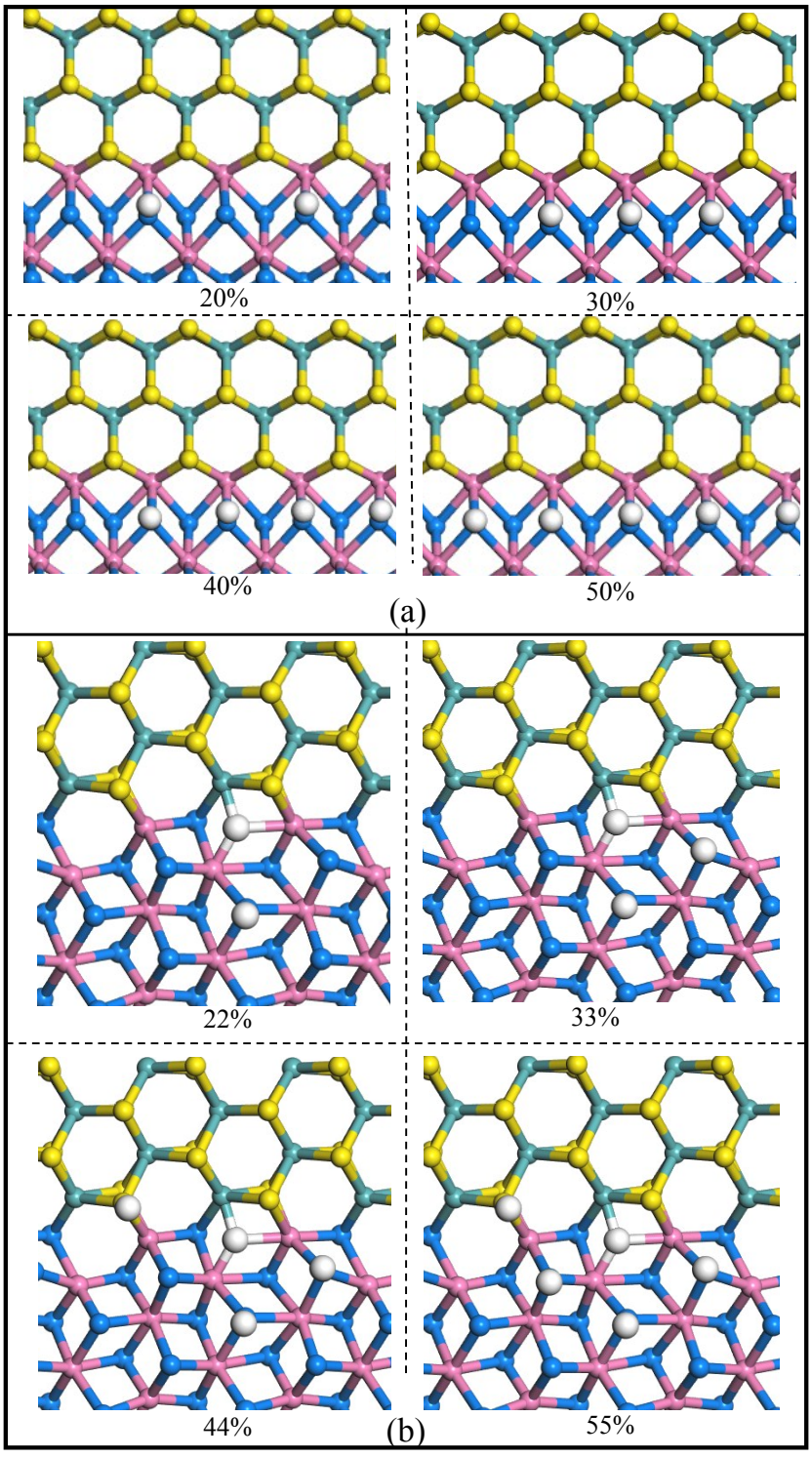

Figure S2. The H adsorption geometries at “Zigzag” (a) and “Armchair” (b) interfaces under different H coverages.

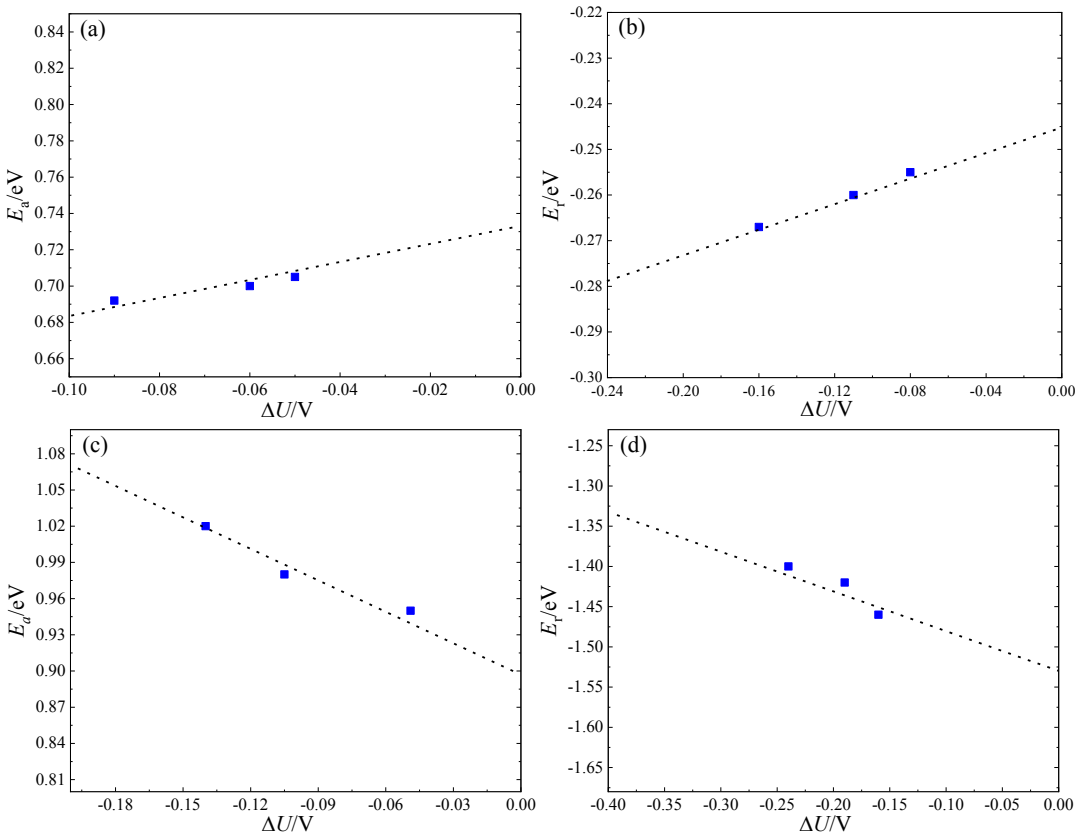

Figure S3. (a) Energy barrier (E_a) and (b) reaction energy (E_r) for the Volmer reaction, (c) E_a and (d) E_r for the Heyrovsky reaction as a function of the change in electrode potential ΔU at the "ZigZag" interface. For the three data points from left to right, the interfacial H coverages in the initial states are 10%, 20% and 30%, respectively.

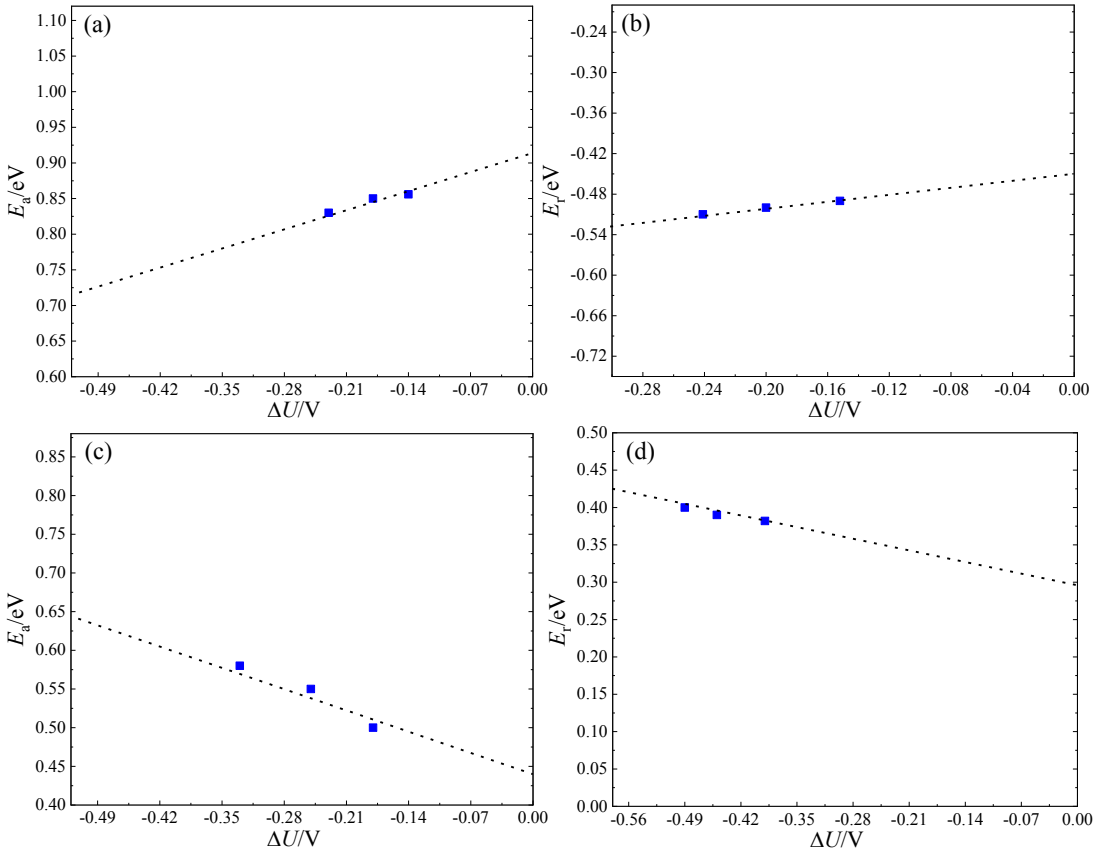

Figure S4. (a) E_a and (b) E_r for the Volmer reaction, (c) E_a and (d) E_r for the Heyrovsky reaction as a function of the change in electrode potential ΔU at the "Armchair" interface. For the three data points from left to right, the interfacial H coverages in the initial states are 11%, 22% and 33%, respectively.

Table S1. The interfacial H adsorption energies (ΔG_H, eV) at 2H phase.

Interface	H-coverage	ΔG_H, eV
Zigzag	10%	0.47
		0.64
		0.77
	20%	0.57
		0.66
		0.87
Armchair	11%	0.60
		0.72
		0.78
	22%	0.64
		0.72
		0.78

Table S2. Free energies (ΔG_H, eV) of H adsorption at the doped "Zigzag" interface.

Dopant	Site	ΔG_H
Co	I	0.59
	II	-0.37
Fe	I	1.23
	II	0.74
Ni	I	0.60
	II	-0.03
Zn	I	0.68
	II	0.58
O	O-H*	-0.94
	I	0.23
	II	0.78
N	N-H*	-1.46
	I	0.05
	II	0.60
P	P-H*	-0.77
	I	0.27
	II	0.87