Electronic Supplementary Information

Doping P Atom with Lone Pair: an Effective Strategy to Realize Considerably High HER Catalytic Activity under a Wide H* Coverage on 2D Silicene and Germanene by Increasing the Structural Rigidity

Wenying Liao[a], Guangtao Yu[*a], Lusi Zhao[a], Hu Zhu[a] and Wei Chen[*a,b]

[a]Engineering Research Center of Industrial Biocatalysis, Fujian Province University, Fujian Provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fujian-Taiwan Science and Technology Cooperation Base of Biomedical Materials and Tissue Engineering, College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, 350007, China

[b]Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen, 361005, China

Email address: yugt@fjnu.edu.cn (G.T. Yu) and chenwei@fjnu.edu.cn (W. Chen)

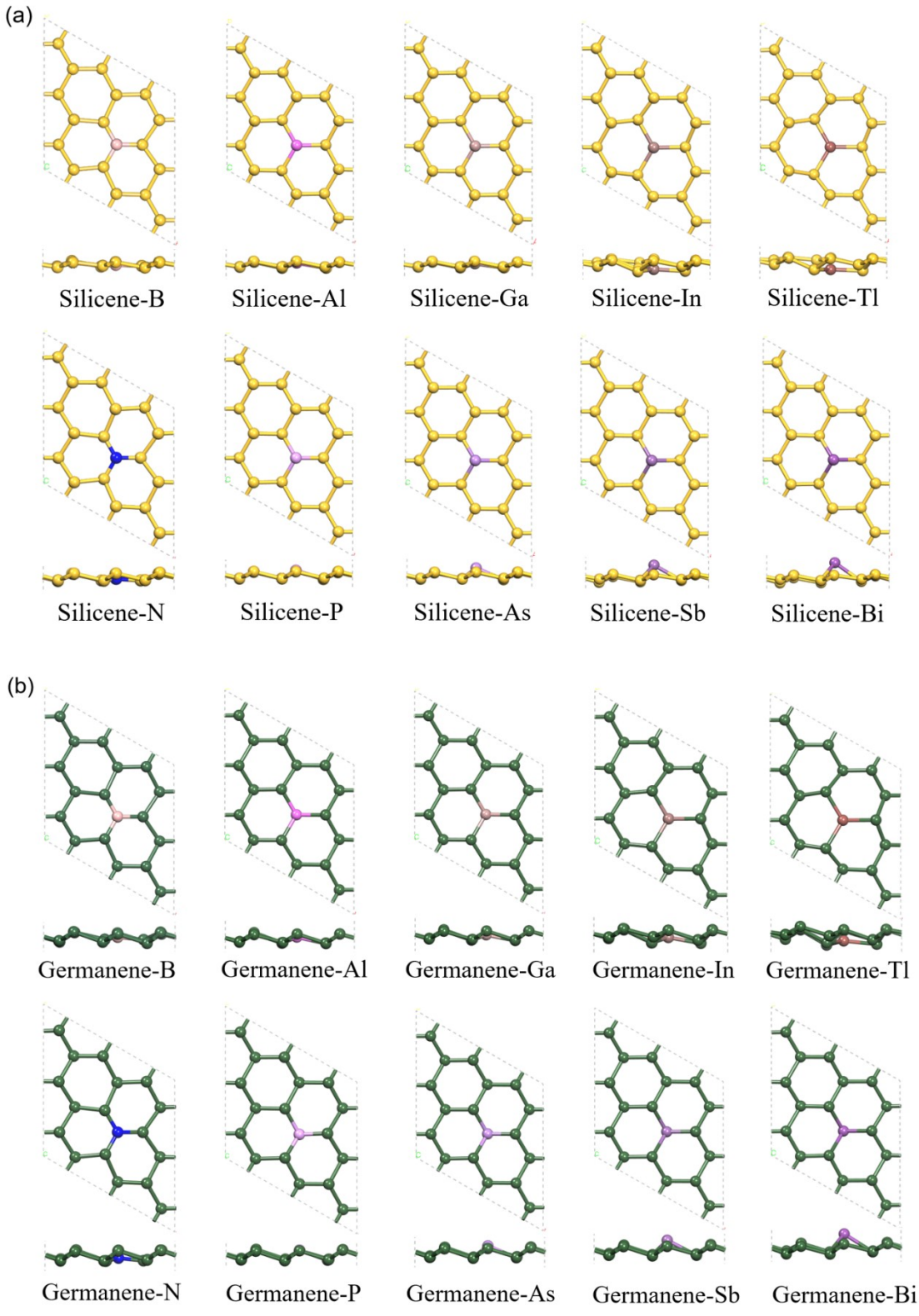

Fig. S1 The top and side views of the optimized structures of Silicene-X (a) and Germanene-X (b) systems (X=B, Al, Ga, In, Tl and N, P, As, Sb, Bi).

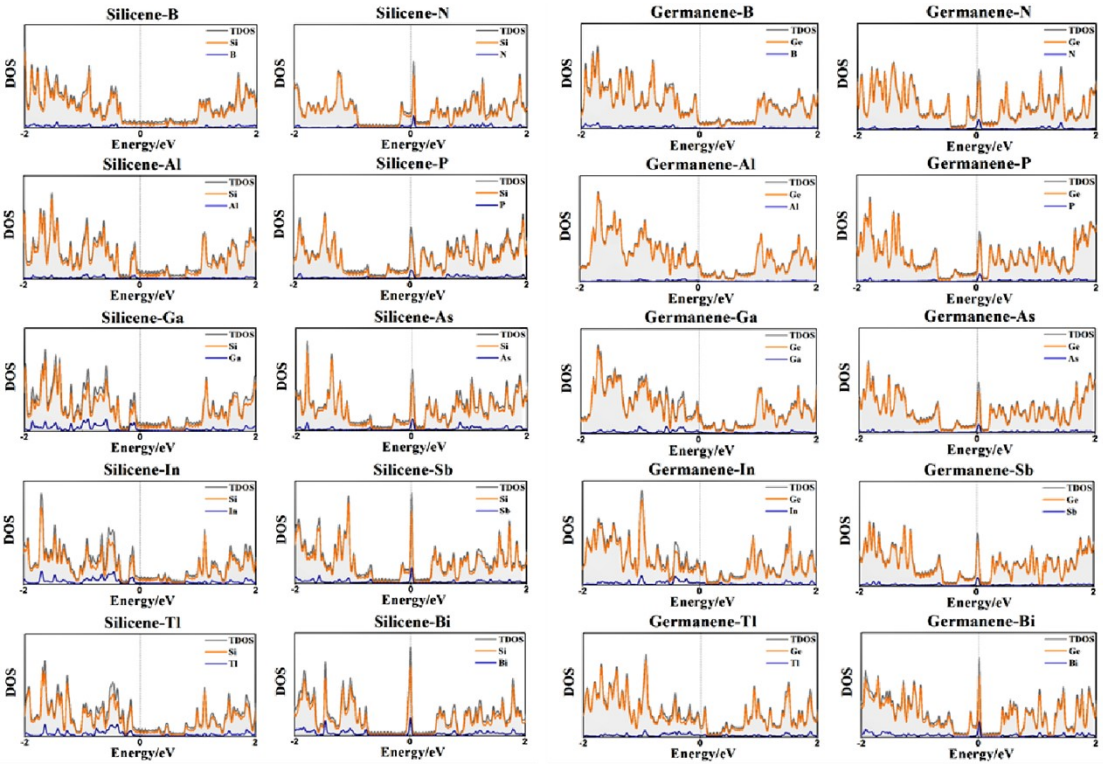

Fig. S2 The calculated DOSs for the Silicene-X and Germanene-X systems.

Table S1 The computed ΔG_{H^*} values in vacuum and in solvation for silicene, germanene, Silicene-P and Germanene-P systems, respectively.

Systems	Adsorption sites	ΔG_{H^*}（eV）	
		in vacuum	in solvation
Silicene	T_{Si}	0.413	0.408
Germanene	T_{Ge}	0.709	0.703
Silicene-P	T_P	0.297	0.269
	T_1	-0.021	-0.030
	T_2	0.028	0.026
	T_3	-0.120	-0.128
	T_4	0.098	0.090
Germanene-P	T_P	0.099	0.094
	T_1	0.093	0.110
	T_2	0.141	0.155
	T_3	0.225	0.228
	T_4	0.451	0.440

Table S2 The calculated ΔG_{H^*} values at the T_X and T_1~T_4 sites for Silicene-X and Germanene-X systems (X=B, Al, Ga, In, Tl and N, P, As, Sb, Bi).

Systems	Lattice constants (Å)	ΔG_{H^*}（eV）				
		T_X	T_1	T_2	T_3	T_4
Silicene-B	11.440	-0.012	0.191	0.153	0.203	0.227
Silicene-Al	11.650	0.359	-0.017	0.238	-0.012	0.266
Silicene-Ga	11.650	0.617	-0.011	0.220	0.001	0.241
Silicene-In	11.650	0.775	-0.066	0.203	-0.008	0.214
Silicene-Tl	11.650	1.553	-0.076	0.157	0.002	0.191
Silicene-N	11.240	0.173	-0.250	-0.004	-0.199	0.055
Silicene-P	11.460	0.297	-0.021	0.028	-0.120	0.098
Silicene-As	11.490	0.582	-0.332	0.071	-0.097	0.157
Silicene-Sb	11.550	0.742	-0.320	0.128	-0.072	0.286
Silicene-Bi	11.550	1.126	-0.344	0.156	-0.094	0.387
Germanene-B	11.870	-0.094	0.402	0.407	0.461	0.552
Germanene-Al	12.070	0.431	0.172	0.524	0.338	0.563
Germanene-Ga	12.070	0.672	0.308	0.528	0.372	0.554
Germanene-In	12.075	1.094	0.279	0.484	0.377	0.527
Germanene-Tl	12.100	1.644	0.353	0.510	0.424	0.520
Germanene-N	11.787	0.030	-0.046	0.213	0.209	0.459
Germanene-P	11.940	0.099	0.082	0.141	0.225	0.451
Germanene-As	11.966	0.404	0.106	0.388	0.246	0.467
Germanene-Sb	12.046	0.554	0.098	0.401	0.233	0.489
Germanene-Bi	12.060	0.924	0.069	0.417	0.230	0.583

Table S3 The angles of H-Si-Si/H-Si-X or H-Ge-Ge/H-Ge-X with the maximum deviation at the adsorption sites corresponding to relatively small absolute ΔG_{H^*} values for the doped Silicene-X and Germanene-X systems.

Systems	Adsorption sites	ΔG_{H^*}（eV）	∠H-Si-Si/H-Si-X
Silicene-B	T_3	0.203	98.2
Silicene-Al	T_3	-0.012	98.4
Silicene-B	T_1	0.191	98.9
Silicene-P	T_3	-0.120	100.9
Silicene-P	T_1	-0.021	101.4
Silicene-Al	T_1	-0.017	101.5
Silicene-Al	T_2	0.238	102.8
Silicene-In	T_2	0.203	103.3
Silicene-N	T_4	0.055	103.5
Silicene-N	T_2	-0.004	104.4
Silicene-Ga	T_3	0.001	105.1
Silicene-In	T_1	-0.066	105.6
Silicene-Tl	T_3	0.002	106.3
Silicene-As	T_4	0.157	114.2
Silicene-P	T_2	0.028	116.0
Silicene-As	T_2	0.071	119.1
Silicene-Sb	T_2	0.128	121.5
Silicene-Bi	T_2	0.156	122.4
Systems	Adsorption sites	ΔG_{H^*}（eV）	∠H-Ge-Ge/H-Ge-X
Germanene-N	T_1	-0.046	98.4
Germanene-N	T_2	0.213	98.5
Germanene-P	T_2	0.141	99.6
Germanene-Al	T_1	0.172	99.9
Germanene-In	T_1	0.279	103.8
Germanene-Bi	T_3	0.230	106.3

Germanene-Sb	T_3	0.233	110.6
Germanene-P	T_3	0.225	114.1
Germanene-Sb	T_1	0.098	114.2
Germanene-As	T_3	0.246	114.6
Germanene-As	T_1	0.106	115.1
Germanene-Bi	T_1	0.069	115.2
Germanene-P	T_1	0.082	115.3
Germanene-N	T_3	0.209	120.2