

Theoretical study of K_3Sb /graphene heterostructure for electrochemical nitrogen reduction reaction

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Supporting Information

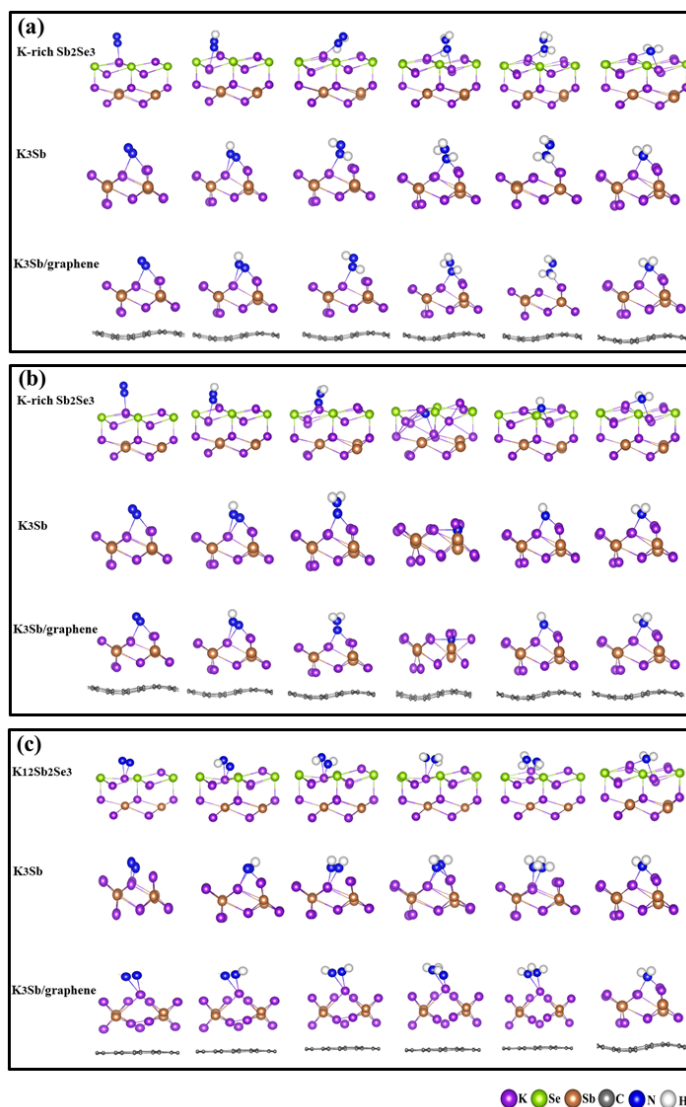


Fig. S1 Calculated reaction sequences for NRR associative and reaction mechanism. (a) and (b) show optimized geometries of intermediates on alternating and distal pathways, (c) presents optimized geometries of enzymatic pathway.



Table S1 Calculated total energy, ZPE and correct energy (G) of intermediates in alternating and distal reaction pathways for $K_{12}Sb_2Se_3$, K_3Sb and $K_3Sb/graphene$. As the unit of eV.

	Alternating			Distal			
	TOTEN Energy	ZPE	G	TOTEN Energy	ZPE	G	
$K_{12}Sb_2Se_3$							
N_2^*	-82.61	0.16	-82.45	N_2^*	-82.61	0.16	-82.45
NNH*	-84.26	0.46	-83.80	NNH*	-84.26	0.46	-83.80
NHNH*	-88.41	0.76	-87.65	NNH ₂ *	-87.70	0.76	-86.94
NHNH ₂ *	-92.09	1.06	-91.03	N*	-71.65	0.08	-71.57
NH ₂ NH ₂ *	-96.84	1.36	-95.48	NH*	-76.49	0.38	-76.11
NH ₂ *	-80.34	0.68	-79.66	NH ₂ *	-80.98	0.68	-80.30
K_3Sb							
N_2^*	-52.71	0.16	-52.55	N_2^*	-52.71	0.16	-52.55
NNH*	-54.72	0.46	-54.26	NNH*	-54.72	0.46	-54.26
NHNH*	-58.66	0.76	-57.90	NNH ₂ *	-57.95	0.76	-57.19
NHNH ₂ *	-62.46	1.06	-61.40	N*	-42.40	0.08	-42.32
NH ₂ NH ₂ *	-66.79	1.36	-65.43	NH*	-45.59	0.38	-45.21
NH ₂ *	-51.38	0.68	-50.70	NH ₂ *	-51.38	0.68	-50.70
$K_3Sb/graphene$							
N_2^*	-515.62	0.16	-515.46	N_2^*	-515.62	0.16	-515.46
NNH*	-518.86	0.46	-518.40	NNH*	-518.86	0.46	-518.40
NHNH*	-522.73	0.76	-521.97	NNH ₂ *	-522.10	0.76	-521.34
NHNH ₂ *	-526.59	1.06	-525.53	N*	-507.06	0.08	-506.98
NH ₂ NH ₂ *	-531.30	1.36	-529.94	NH*	-510.11	0.38	-509.73
NH ₂ *	-515.42	0.68	-514.74	NH ₂ *	-515.42	0.68	-514.74
NH ₂ *	-515.62	0.68	-515.46	NH ₂ *	-515.62	0.68	-515.46

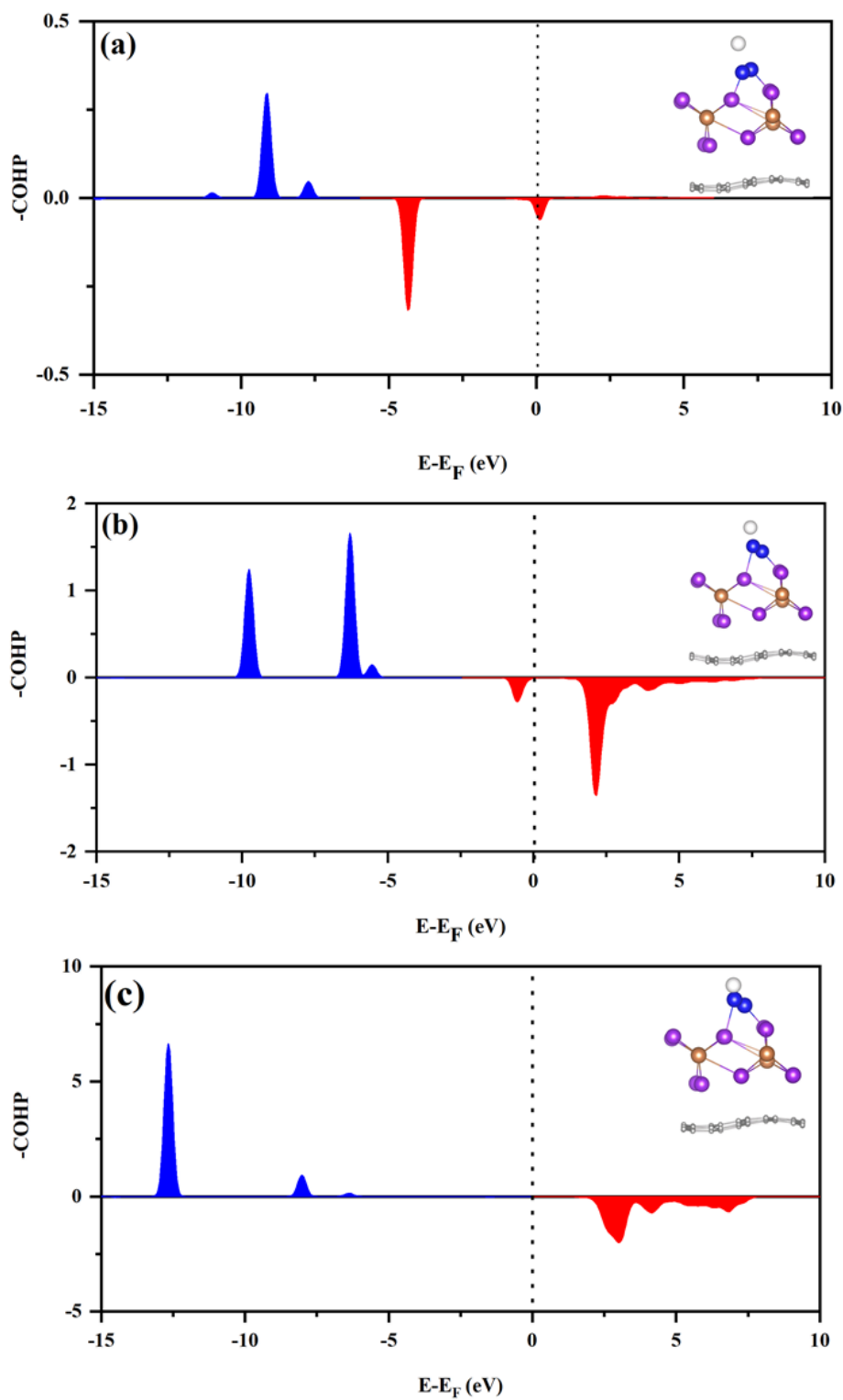


Fig. S2 Evolution of the -COHP for the N-H bond formation on K_3Sb/G . The inserted pictures are side view of (a) initial state, (b) the transition state, and (c) the final state structures of $N_2^* + H^* \rightarrow NNH^*$ are shown.

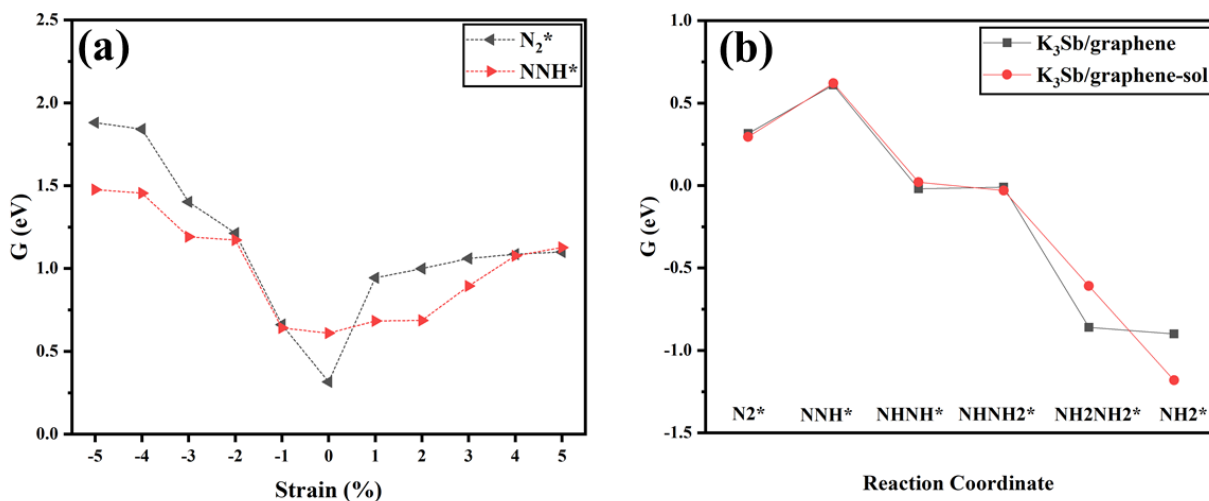


Fig. S3 The influence of strain effect and solvent effect on reaction coordinate of $K_3Sb/graphene$. (a) shows the Gibbs free energy difference of N_2 adsorption and the first H^* addition under strain effect. (b) shows the Gibbs free energy difference of intermediates via alternating pathway under solvent effect.

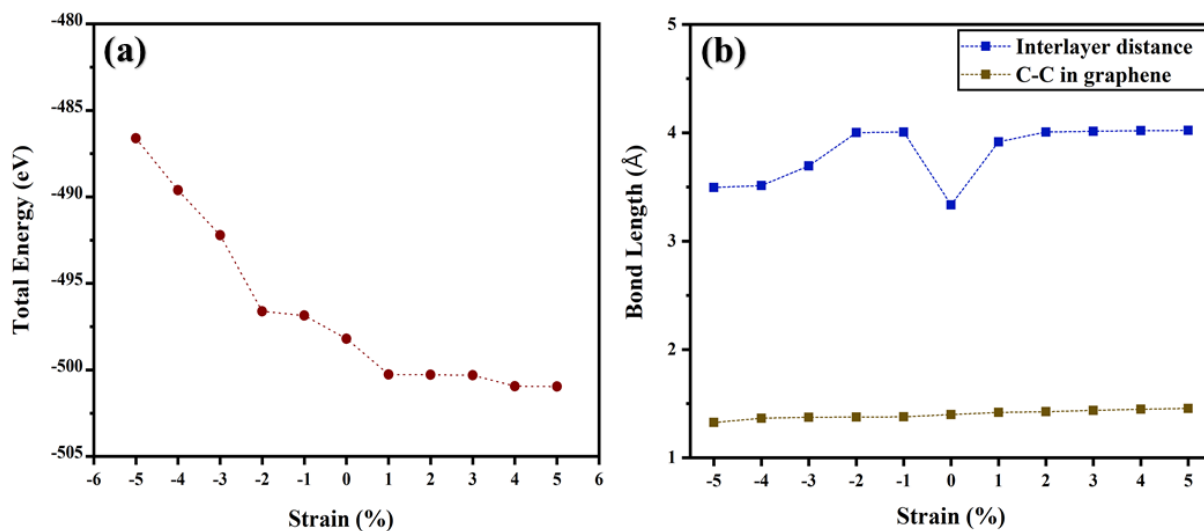


Fig. S4 The influence of biaxial strain on $K_3Sb/graphene$. (a) Total energy of perfect $K_3Sb/graphene$, (b) C-C bond length of graphene and interlayer distance between graphene and K_3Sb .

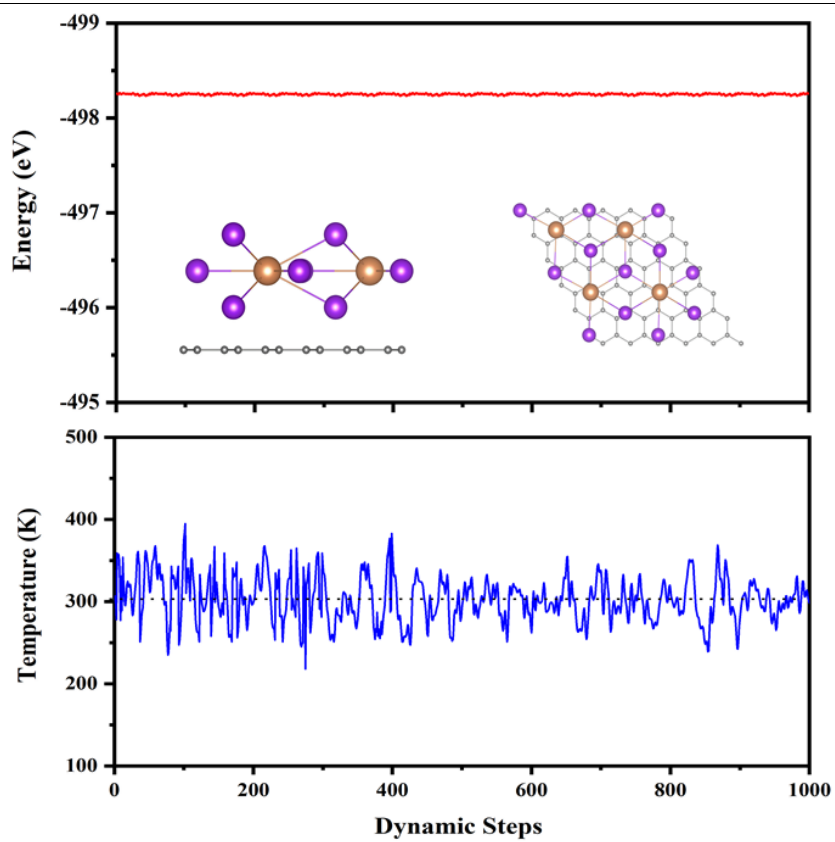


Fig. S5 Energy and temperature fluctuations of K₃Sb/graphene during AIMD simulation. The insets illustrate the top view and side view of K₃Sb/graphene structure after 2 ps of AIMD simulation at $T = 300$ K.