Electronic Supplementary Information (ESI) for

Defective 2D Silicon Phosphide Monolayers for Electrochemical Nitrogen Reduction Reaction: A DFT Study

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1. 2D SiP structures

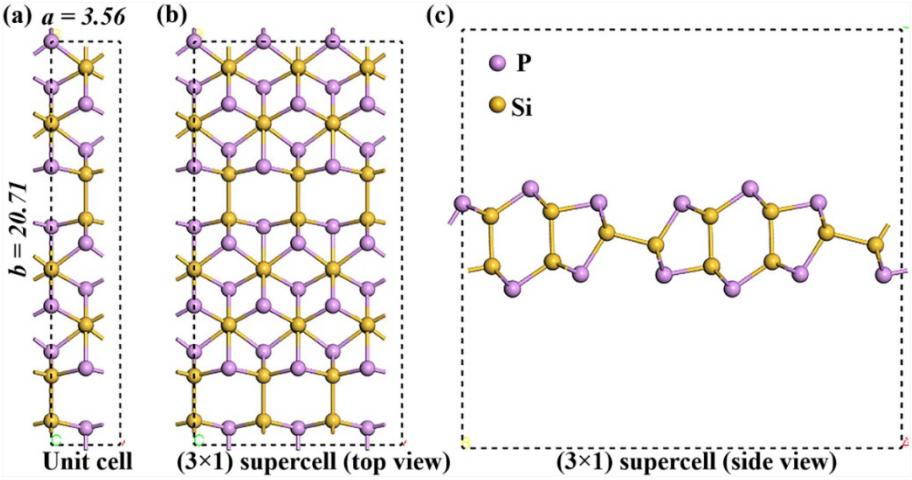

Fig. S1. Optimized unit cell and supercell of 2D SiP. Color scheme: Si (yellow), P (purple).

2. N_2 adsorption on 2D SiP

Fig. S2. Physisorption interaction between N_2 and 2D pristine SiP. Color scheme: Si (yellow), P (purple), and N (blue).

3. Characteristics of defective SiP

Table S1. Binding energies of surface P atoms and formation energies of defective SiP

Potential defective sites	Binding energies (E_b) of P in different positions/eV	Defective SiP catalysts	Fromation energes (E_f) of Dn-SiP (n = 1, 2, and 3)/eV
D1	-6.72	D1-SiP	2.89
D2	-6.75	D2-SiP	2.50
D3	-6.58	D3-SiP	2.59

Table S2. Charges and spin of Si atoms on defective sites of 2D SiP

Defective SiP	**Defective sites**	**Mulliken charges/|e|**	**Spin/hbar**	**Hirshfeld charges/|e|**	**Spin/hbar**
D1-SiP	Si1	+0.14	-0.02	+0.06	0.00
	Si2	+0.17	+0.12	+0.06	+0.08
	Si3	+0.17	+0.12	+0.06	+0.08
D2-SiP	Si1	+0.09	0.00	+0.04	0.00
	Si2	+0.16	0.00	+0.06	0.00
	Si3	+0.16	0.00	+0.06	0.00
D3-SiP	Si1	+0.15	+0.02	+0.06	0.00
	Si2	+0.16	-0.08	+0.06	-0.06
	Si3	+0.16	-0.08	+0.06	-0.06

4. PDOS of Si atoms on defective sites

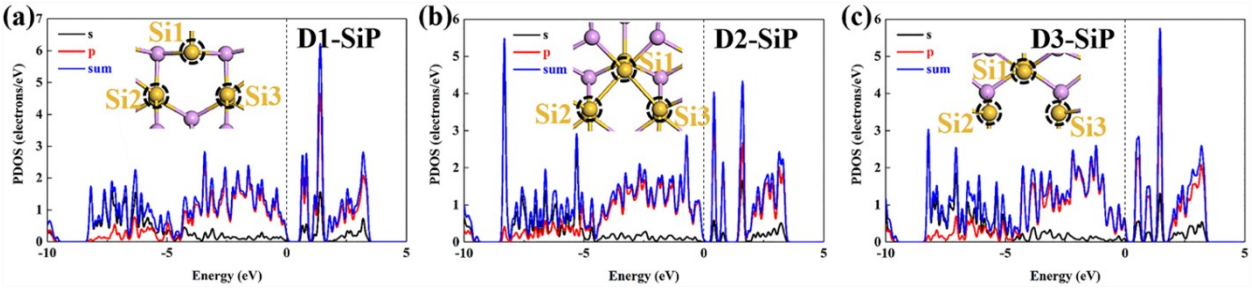

Fig. S3. PDOS of Si atoms on defective sites of 2D SiP, including the s and p-orbital contributons. Inserts in Figures are the schematic diagram of active Si atoms (named as Si1, Si2 and Si3) around the P-defects. Color scheme: Si (yellow), P (purple). Color scheme: Si (yellow), P (purple).

5. Charge analysis for $*N_2$ on defective SiP

Table S3. Charges and spin analyses for chemically adsorbed $*N_2$ on 2D SiP

Catalysts	Mulliken charges/|e|	Spin/hbar	Hirshfeld charges/|e|	Spin/hbar
D1-SiP	-1.33	0.40	-0.36	0.34
D2-SiP	-1.39	-0.40	-0.32	-0.33
D3-SiP	-1.34	0.39	-0.36	0.33

6. ΔG_{max}^{NRR} vs. ΔG_{max}^{HER} on D1-SiP

Table S4. Maxmium free energy analyses for NRR and HER, respectively, under $U_{applied}$ = 0 V and $U_{applied}$ = -0.87 V

Reaction pathways	ΔG_{max}^{NRR}		Adsorption species	ΔG_{max}^{HER}	
	U = 0 V	U = -0.87 V		U = 0 V	U = -0.87 V
Path1 (consecutive)	1.17 eV	0.30 eV	*H_1	0.22 eV	1.09 eV
Path2 (enzymatic)	1.25 eV	0.38 eV			
Path3 (consecutive)	1.38 eV	0.51 eV	*H_2	0.63 eV	1.50 eV
Path4 (enzymatic)	0.87 eV	0.00 eV			

7. H_2O adsorption on D1-SiP

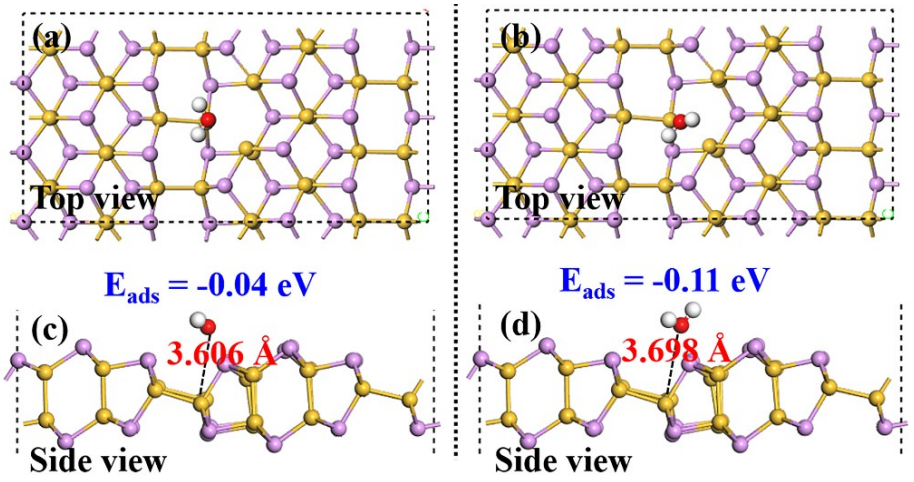

Fig. S4 The top (a & b) and side views (c & d) of two different physioadsorption configurations of H_2O on D1-SiP. Color scheme: Si (yellow), P (purple), O (red), and H (white).

8. DOS analysis for adsorbed N_2 on D1-SiP

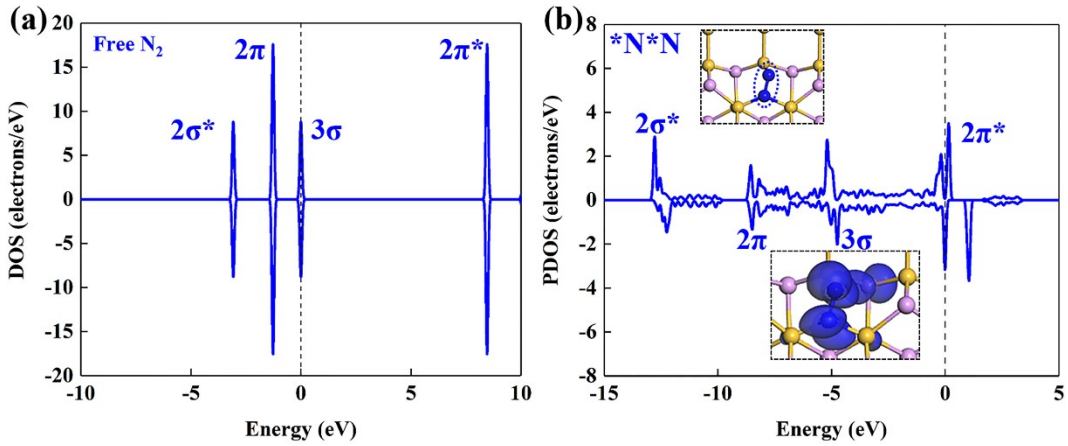

Fig. S5 DOS analysis for (a) the free N_2 molecule and (b) *N*N on D1-SiP. Inserts are the strucutre image and the corresponding spin density (Isosurface: 0.01 a.u.). Color scheme: Si (yellow), P (purple), and N (blue).

9. N-N bond evolution along the optimal pathway (Path4)

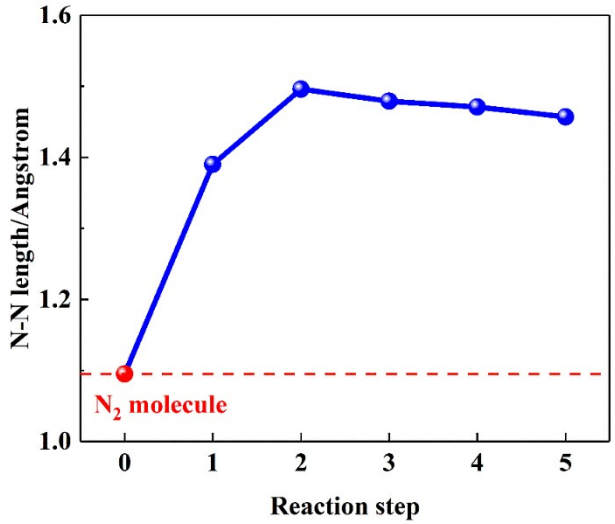

Fig. S6 The N-N bond evolution along the Path4. The dash line indicates the level of N-N bond length of a free N_2 molecule. Step1 suggests the adsorption step of N_2, then step2-step5 indicate the hydrogenation processes.

10. AIMD simulation of D1-SiP

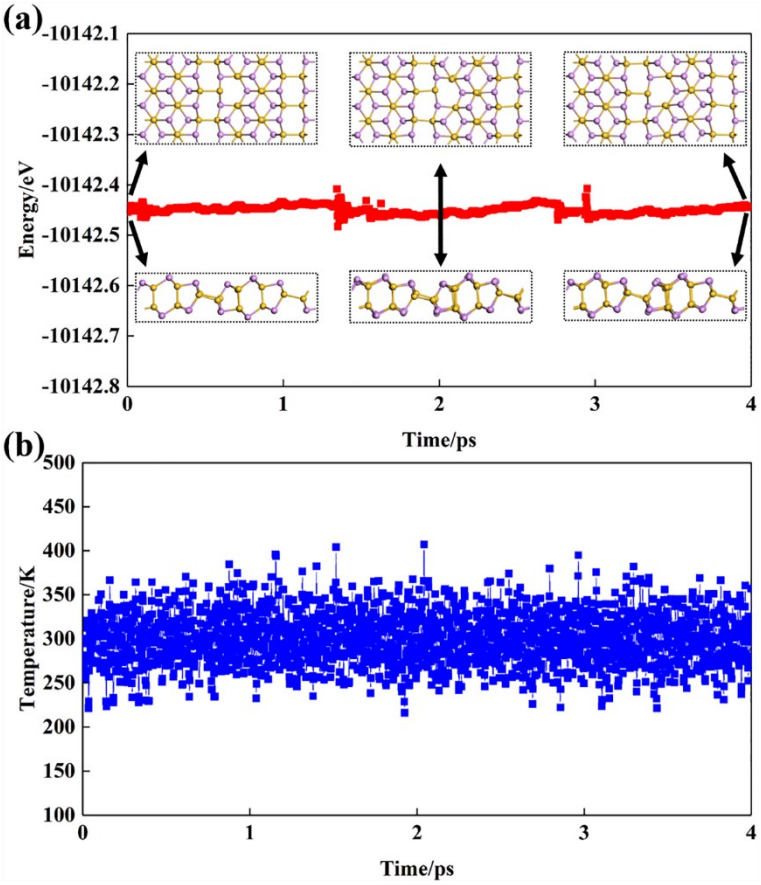

Fig. S7 Variations of (a) energy and (b) temperature of the defective D1-SiP system against the time in the AIMD simulation at 300 K for 4 ps with a time step of 2 fs. Color scheme: Si (yellow), P (purple).

11. Density functional theory data

11.1 Thermochemistry of $0.5N_2 + 1.5H_2 \rightarrow NH_3$

The Gibbs free energy calculation was performed as follows:

$$\Delta\mu = \Delta E_{\mathrm{DFT}} + \Delta E_{ZPE} - T\cdot\Delta S \quad (1)$$

where μ, E_{DFT}, and E_{ZPE} represent the chemical potential (Gibbs freeenergy per molecular), electronic energy, and zero-point energy, respectively. The entropy (S) consists of the translational (S_t), rational (S_r), vibrational (S_v) and electronic contributions (S_e) and thus can be expressed as:

$$S = S_t + S_r + S_v + S_e \quad (2)$$

where S_e is around zero at the foundamental electronic level.

Gases	E_{DFT}/eV [a]	ZPE/eV [b]	$-T \cdot S$ [c]	μ
H_2 (g)	-32.04	0.27	-0.40	-32.17
N_2 (g)	-539.86	0.15	-0.59	-540.30
NH_3 (g)	-318.89	0.89	-0.60	-318.60

[a] Obtained from DFT calculations.

[b, c] Obtained from the NIST database (https://cccbdb.nist.gov).

11.2 Test calculations of K-point sets

Table S5. Test calculations of K-point set

Species	Electronic energies/eV		
	(3×1×1)	(3×2×1)	(3×3×1)
D1-SiP	-10145.34	-10145.36	-10145.36
*N*N	-10685.47	-10685.50	-10685.50
*N*NH	-10702.99	-10703.02	-10703.02
NNH_2	-10717.96	-10717.98	-10717.98
*NH*NH	-10718.01	-10718.04	-10718.04

11.3 Corrected free energy of intermediates

Table S6. Corrected free energies for NRR intermediates along path1

Reaction species	E_{DFT}/eV	E_{ZPE}/eV	-T·S/eV	G/eV	ΔG_i/eV
D1-SiP (*)	-10145.34	4.09	-4.36	-10145.61	—
*N*N	-10685.47	4.35	-4.43	-10685.55	0.36
*N*NH	-10702.99	4.68	-4.39	-10702.70	-1.06
NNH_2	-10717.96	4.97	-4.62	-10717.61	1.17
*N	-10418.12	4.26	-4.35	-10418.21	-3.12
*NH	-10433.28	4.52	-4.42	-10433.18	1.12
*NH_2	-10448.95	4.84	-4.47	-10448.58	0.69
*NH_3	-10464.48	5.16	-4.52	-10463.84	0.82
NH_3	-318.89	0.89	-0.60	-318.60	-0.37

Table S7. Corrected free energies for NRR intermediates along path2

Reaction species	E_{DFT}/eV	E_{ZPE}/eV	-T·S/eV	G/eV	ΔG_i/eV
D1-SiP (*)	-10145.34	4.09	-4.36	-10145.61	—
*N*N	-10685.47	4.35	-4.43	-10685.55	0.36
*N*NH	-10702.99	4.68	-4.39	-10702.70	-1.06
*NH*NH	-10718.01	4.93	-4.45	-10717.53	1.25
NHNH_2	-10733.54	5.28	-4.47	-10732.73	0.89
*NH_2*NH_2	-10749.22	5.58	-4.64	-10748.28	0.54
*NH_2	-10448.95	4.84	-4.47	-10448.58	-2.82
*NH_3	-10464.48	5.16	-4.52	-10463.84	0.82
NH_3	-318.89	0.89	-0.60	-318.60	-0.37

Table S8. Corrected free energies for NRR intermediates along path3

Reaction species	E_{DFT}/eV	E_{ZPE}/eV	-T·S/eV	G/eV	ΔG_i/eV
D1-SiP (*)	-10145.34	4.09	-4.36	-10145.61	—
*N*N	-10685.47	4.35	-4.43	-10685.55	0.36
*NH*N	-10701.88	4.69	-4.43	-10701.62	0.02
*NH_2*N	-10717.96	4.99	-4.49	-10717.46	0.24
*N	-10418.12	4.26	-4.35	-10418.21	-3.27
*NH	-10433.28	4.52	-4.42	-10433.18	1.12
*NH_2	-10448.22	4.80	-4.47	-10447.89	1.38
*NH_3	-10464.23	5.14	-4.46	-10463.55	0.43
NH_3	-318.89	0.89	-0.60	-318.60	-0.66

Table S9. Corrected free energies for NRR intermediates along path4

Reaction species	E_{DFT}/eV	E_{ZPE}/eV	-T·S/eV	G/eV	ΔG_i/eV
D1-SiP (*)	-10145.34	4.09	-4.36	-10145.61	—
*N*N	-10685.47	4.35	-4.43	-10685.55	0.36
*NH*N	-10701.88	4.69	-4.43	-10701.62	0.02
*NH*NH	-10717.85	4.98	-4.48	-10717.35	0.35
*NH_2*NH	-10733.34	5.29	-4.52	-10732.57	0.87
*NH_2*NH_2	-10749.22	5.58	-4.64	-10748.28	0.38
*NH_2	-10448.22	4.80	-4.47	-10447.89	-2.13
*NH_3	-10464.23	5.14	-4.46	-10463.55	0.43
NH_3	-318.89	0.89	-0.60	-318.60	-0.66