Supporting Information

B-Terminated (111) Polar Surface of BP and BAs: Promising Metal-Free Electrocatalysts with Large Reaction Regions for Nitrogen Fixation

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Table S1. Calculated BAs (111) surface energies with different layers and its adsorption energies of N_2 by side-on pattern.

Slab layers	Surface energy (J/m^2)	Adsorption energy (eV)
3	2.10	-0.301
4	2.21	-0.558
5	2.22	-0.564
6	2.23	-0.576

Table S2. Calculated surface energies (J/m^2) of BP and BAs.

Crystal		Surface	Surface energy (γ_s)
BP	(100)	B-terminated	2.78
		P-terminated	3.71
	(110)	B/P-terminated	2.71
	(111)	B-terminated	2.75
		P-terminated	2.95
BAs	(100)	B-terminated	1.99
		As-terminated	3.00
	(110)	B/As-terminated	2.18
	(111)	B-terminated	2.21
		As-terminated	2.37

Table S3. Calculated adsorption free energies (eV) of N_2 molecule with side-on and end-on patterns on (100), (110) and (111) surfaces of BP and BAs.

configuration	BP			BAs		
	(100)	(110)	(111)	(100)	(110)	(111)
side-on	0.35	0.46	0.11	0.47	0.47	0.08
end-on	-0.02	0.07	0.02	-0.03	-0.16	-0.10

Table S4. The calculated vibrational frequency, zero point energy and entropic corrections of various NRR reaction intermediates on the (111) polar surfaces, where the * denotes the adsorption site, and *N-N* and *N-N represent the side-on and end-on adsorption configurations, respectively. The ΔZPE and $T\Delta S$ for each reaction intermediates can be calculated by the following equations, respectively:

$$\Delta ZPE = \frac{1}{2}\sum_i h\nu_i$$

$$T\Delta S = \sum_i \left(\frac{h\nu_i}{e^{\frac{h\nu_i}{K_B T}} - 1} \right) - K_B T \sum_i \ln\left(1 - e^{-\frac{h\nu_i}{K_B T}}\right)$$

in which h, ν and K_B are Planck constant, vibrational frequency and Boltzmann constant, respectively. Only the zero point energy and the entropic corrections of the adsorption species are calculated because the contribution of the substrate can be offset.

	Adsorption species	Vibrational Frequencies (cm^{-1})						ΔZPE (eV)	$T\Delta S$ (eV)
BP	*N-N*	1395.35	614.31	479.77	420.46	278.52	180.62	0.21	0.07
	N-NH	3423.02	1395.10	1124.10	720.13	680.79	550.19	0.55	0.06
		402.49	351.70	192.47					
	NH-NH	3525.22	3502.54	1402.89	1290	902.562	763.516	0.82	0.12
		613.814	411.965	319.278	234.192	199.653	108.324		
	NH-NH_2	3435.01	3386.21	3315.52	1542.85	1402.38	1256.17	1.21	0.09
		1198.49	820.56	756.96	729.37	538.88	483.55		
		329.868	202.84	146.70					
	NH_2+NH_2	3571.94	3563.67	3478.16	3465.45	1564.03	1552.78	1.40	0.18
		928.37	920.25	704.58	688.53	500.09	425.66		
		311.65	221.14	204.59	195.51	184.56	124.19		
	NH_2+NH_3	3477.90	3420.37	3396.78	3351.34	2571.33	1628.72	1.80	0.13
		1571.26	1553.94	1406.45	995.82	985.21	912.20		
		821.26	619.95	550.77	497.59	345.25	284.31		
		226.44	195.95	183.65					
	*N-N	2178.70	450.99	411.72	410.43	101.92	82.01	0.22	0.13
	*N-NH	3145.61	1565.67	1367.06	847.63	575.05	381.63	0.51	0.15
		248.31	105.77	45.53					
	*NH-NH	3360.43	3327.09	1477.83	1301.77	1190.90	788.47	0.81	0.16
		626.23	475.61	360.12	111.98	93.04	75.54		
	*N-NH_2	3424.22	2645.25	1589.08	1298.90	1219.29	721.09	0.81	0.11

		633.13	617.68	391.37	340.09	135.48	104.18		
	*NH-NH_2	3428.78 1117.96 262.08	3417.93 879.08 128.58	3262.99 702.32 37.18	1601.14 534.49	1429.14 331.65	1216.75 293.34	1.15	0.17
	*NH_2-NH_2	3445.12 1386.12 549.15	3294.92 1269.80 315.12	3238.66 1226.33 282.68	3185.75 1089.04 186.35	1626.39 891.42 146.97	1572.74 830.85 110.21	1.53	0.15
	*N	701.35	159.55	140.96				0.06	0.07
	*NH	3419.48	850.82	716.73	356.99	178.38	158.42	0.35	0.08
	*NH_2	3566.47 267.80	3478.76 192.97	1560.00 168.69	924.25	701.33	474.02	0.70	0.09
	*NH_3	3393.88 879.11	3379.18 869.75	3282.48 517.65	1582.69 198.20	1579.11 182.27	1345.08 170.24	1.08	0.09
	N-N	1346.37	587.42	485.56	431.89	326.39	186.11	0.21	0.07
	N-NH	3436.99 417.43	1402.17 360.87	1092.76 194.12	713.23	659.75	559.85	0.55	0.06
	NH-NH	3486.29 699.00	3423.55 518.82	1358.78 495.15	1335.74 393.75	929.05 248.63	771.03 213.67	0.86	0.07
	NH-NH_2	3443.05 1198.45 333.16	3381.69 812.18 207.17	3317.92 733.59 178.82	1549.98 726.03	1402.73 524.56	1258.81 452.08	1.21	0.09
	NH_2+NH_2	3574.64 915.28 312.57	3569.87 909.36 222.19	3484.81 716.82 209.94	3479.29 703.45 207.65	1565.60 468.06 193.37	1559.03 412.38 162.61	1.40	0.18
	NH_2+NH_3	3483.19 1580.56 803.92 227.82	3408.45 1560.33 634.21 197.28	3404.11 1413.56 541.93 173.74	3344.24 989.56 484.68	2716.79 982.25 343.55	1622.29 913.15 265.98	1.80	0.13
BAs	*N-N	2158.95	465.55	428.33	421.83	95.59	75.36	0.23	0.13
	*N-NH	3127.03 257.71	1556.45 77.38	1374.60 53.20	833.97	574.26	375.02	0.51	0.15
	*NH-NH	3370.44 628.83	3286.34 565.57	1513.88 370.47	1320.42 127.46	1244.90 77.83	880.27 45.51	0.83	0.17
	*N-NH_2	3534.09 532.21	3278.58 412.12	1612.15 360.37	1315.35 150.40	1209.95 127.01	606.07 59.25	0.81	0.16
	*NH-NH_2	3443.28 1116.10 163.94	3430.39 862.52 111.78	3344.03 701.05 72.29	1615.97 511.48	1412.18 330.59	1250.15 235.63	1.14	0.17
	*NH_2-NH_2	3444.39 1385.06 547.44	3305.73 1266.22 302.31	3238.68 1238.89 221.68	3195.19 1093.57 193.03	1630.23 873.69 129.47	1576.43 836.42 82.07	1.52	0.16
	*N	749.05	135.79	122.96				0.06	0.08
	*NH	3496.77	875.45	632.40	333.66	180.78	168.62	0.35	0.08
	*NH_2	3569.61	3484.60	1562.11	908.92	724.21	443.49	0.70	0.09

		268.86	193.67	186.71					
	*NH_3	3386.80 890.07	3363.72 881.02	3280.22 519.24	1587.64 213.13	1584.85 182.15	1364.09 172.60	1.08	0.09

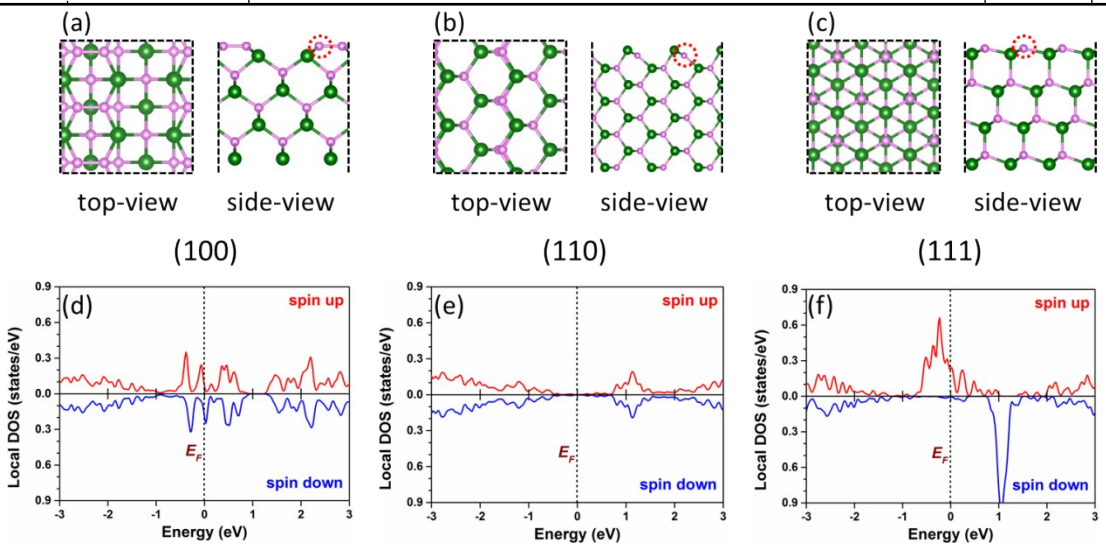

Figure S1. Schematic atomic structures of (a) the (100) surface, (b) the (110) surface, and (c) the (111) surface of cubic BAs. The local density of states (LDOS) of surface B atoms marked by red dashed circle on (d) the (100) surface, (e) the (110) surface, and (f) the (111) surface of cubic BAs. The Fermi level (E_F) was set to be zero and denoted by the black dashed line.

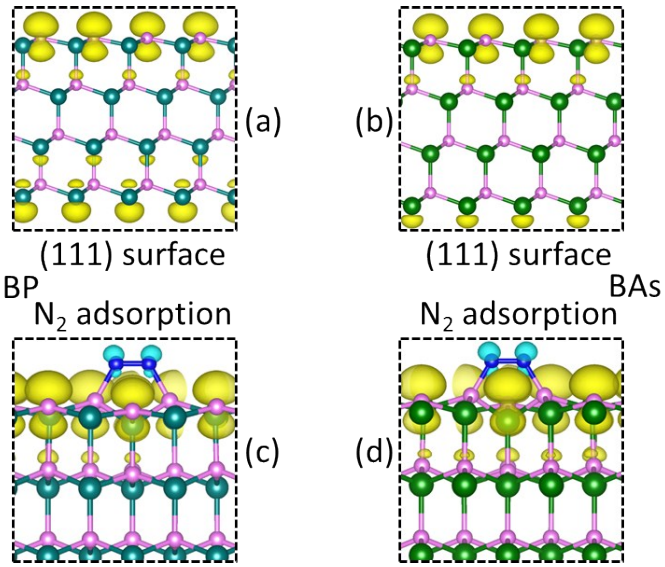

Figure S2. The spin density of the (111) surface of (a) BP and (b) BAs, and the corresponding N_2 adsorption by side-on pattern (c) and (d), in which the isosurface value is set to be 0.006 e $Å^{-3}$.

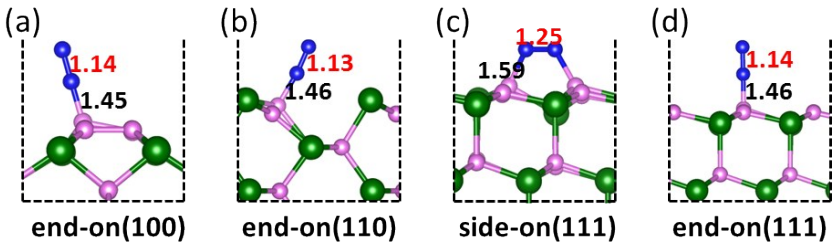

Figure S3. Schematic diagram of all stable nitrogen adsorption configurations in (a) the (100) surface, (b) the (110) surface, (c) and (d) the (111) surface of BAs, in which the red value is N-N bond length, and the black value is B-N bond length (Å).

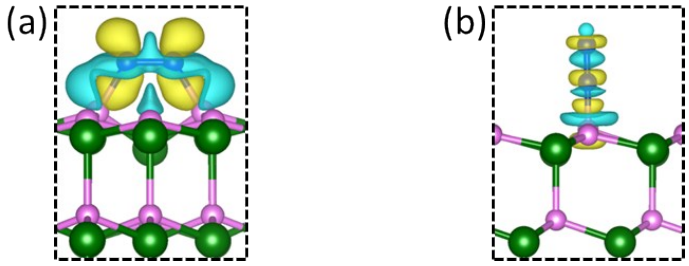

Figure S4. Difference charge density of BAs (111) surface with the adsorption of N_2 via (a) side-on pattern and (b) end-on pattern, where the isosurface value is set to be 0.005 e $Å^{-3}$, and cyan and yellow regions represent positive and negative charges, respectively.

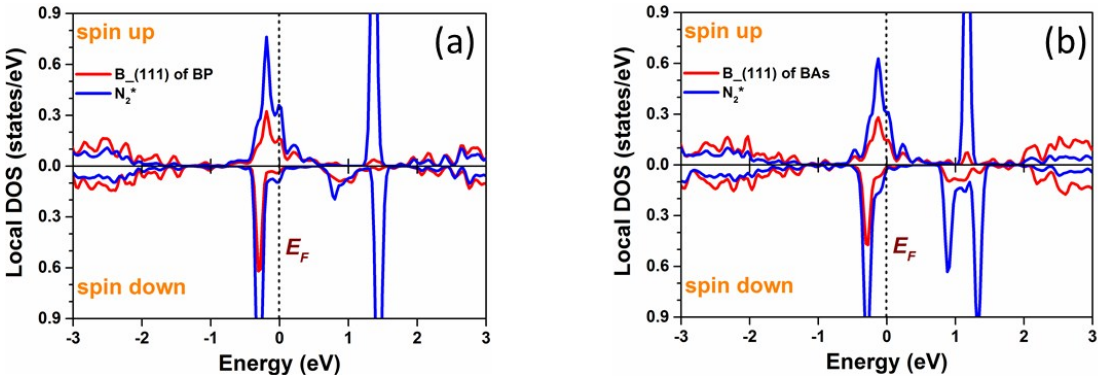

Figure S5. The LDOS of B atom in (111) surface after N_2 adsorption by side-on pattern, (a) BP and (b) BAs. The Fermi level (E_F) was set to be zero as denoted by the black dashed line.

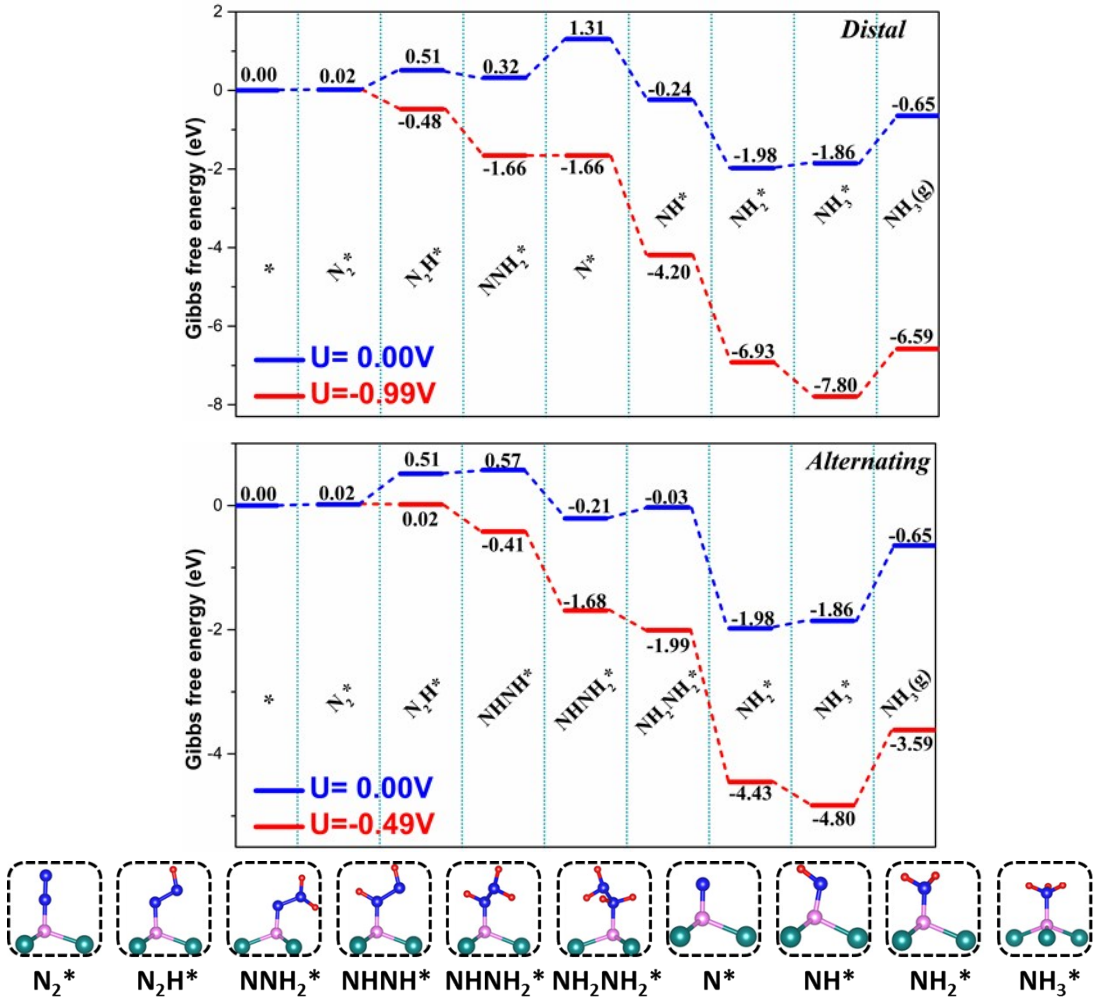

Figure S6. Gibbs free energy diagrams for N_2 reduction through distal and alternating mechanisms on the BP (111) surface at zero and applied potentials. The corresponding reaction intermediates are given in the lower panel.

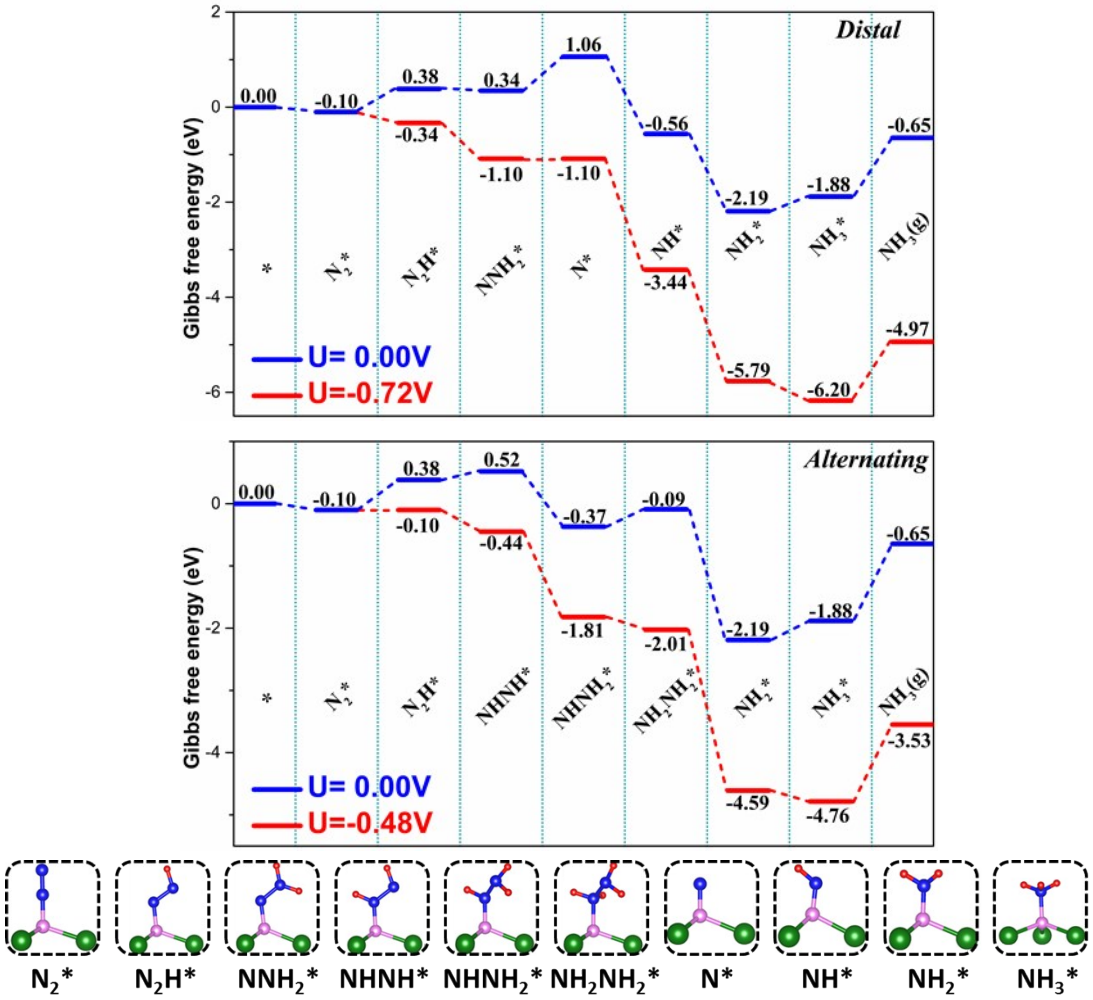

Figure S7. Gibbs free energy diagrams for N_2 reduction through distal and alternating mechanisms on BAs (111) surface at zero and applied potentials. The corresponding reaction intermediates are given in the lower panel.

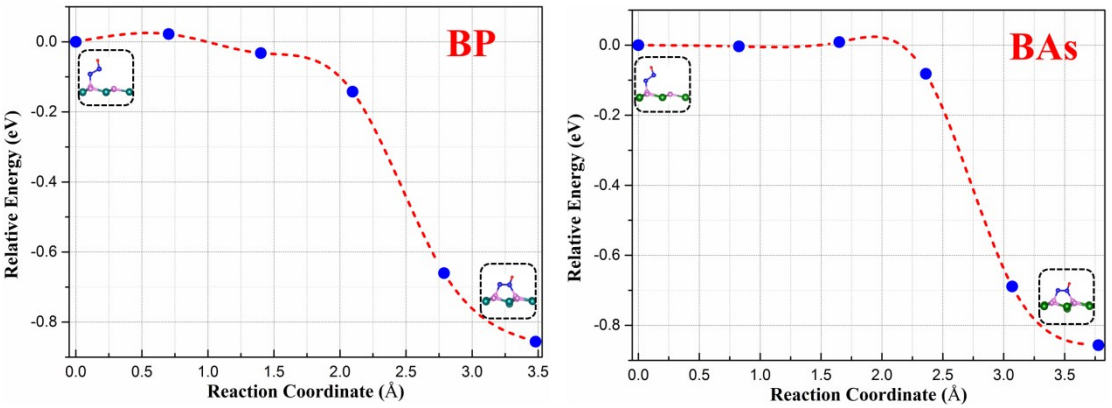

Figure S8. The minimum reaction pathway for N_2H^* species from the end-on configuration to the side-on configuration on (a) BP and (b) BAs.

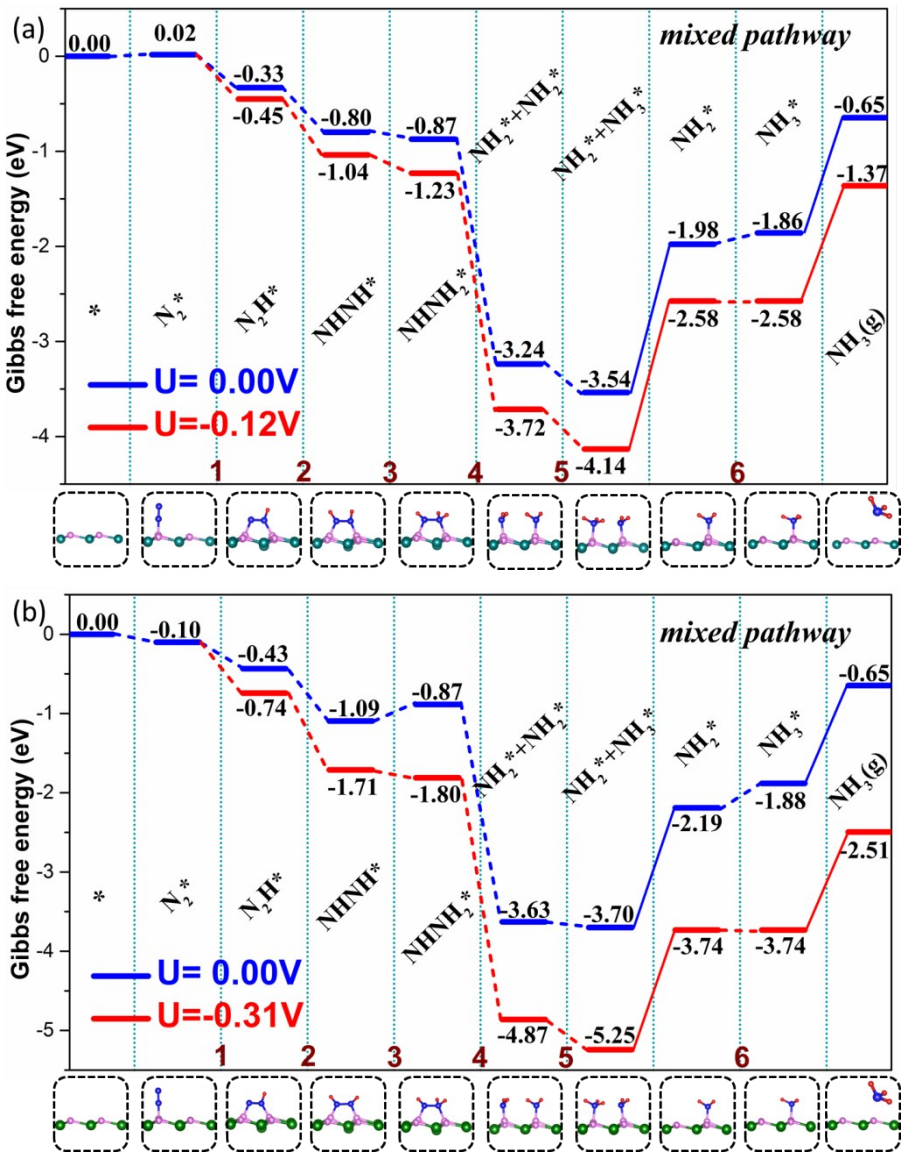

Figure S9. Gibbs free energy diagrams for N_2 reduction through mixed pathways on (a) BP (111) surface and (b) BAs (111) surface at zero and applied potentials. The corresponding reaction intermediates are given in the lower panel.

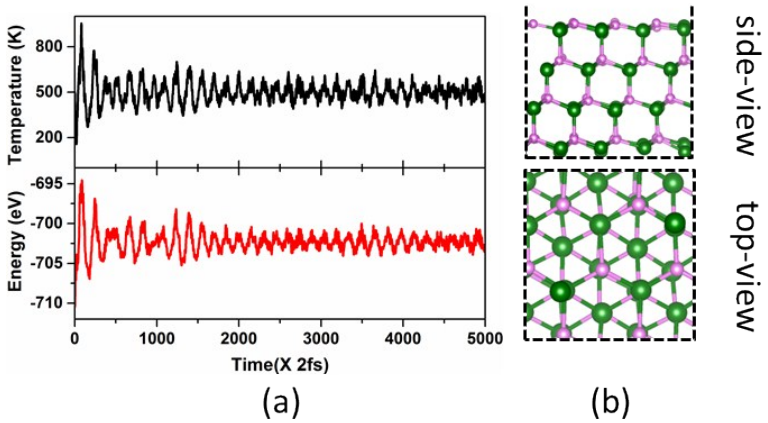

Figure S10. (a) Variations of temperature and energy of the BAs (111) surface vs the AIMD simulation. (b) Schematic diagram of the structure after dynamics simulation.