Electronic Supplementary Information

Electroreduction of N_2 to ammonia at ambient conditions on mononitrides of Zr, Nb, Cr, and V – A DFT guide for experiments

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DFT calculations are used to find the adsorption energy of the most stable intermediates along the reaction path by considering all the possible adsorption sites of proton on the surface. To construct free energy diagrams, the free energy of each elementary step is estimated at pH = 0 according to:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \qquad (1)$$

where ΔE is the reaction energy calculated using DFT. The zero-point energy correction (ΔE_{ZPE}) and entropy difference (ΔS) are calculated within a harmonic approximation (given in table S1 below). The effect of an applied bias, U, is included for all electrochemical reaction steps by shifting the free energy for reactions involving n electrons by $-neU$:

$$\Delta G(U) = \Delta E + \Delta E_{ZPE} - T\Delta S - neU \qquad (2)$$

Table S1. Zero point energy and entropy contributions to the free energy of gas phase and adsorbed molecules at 300 K for RS nitrides (in eV).
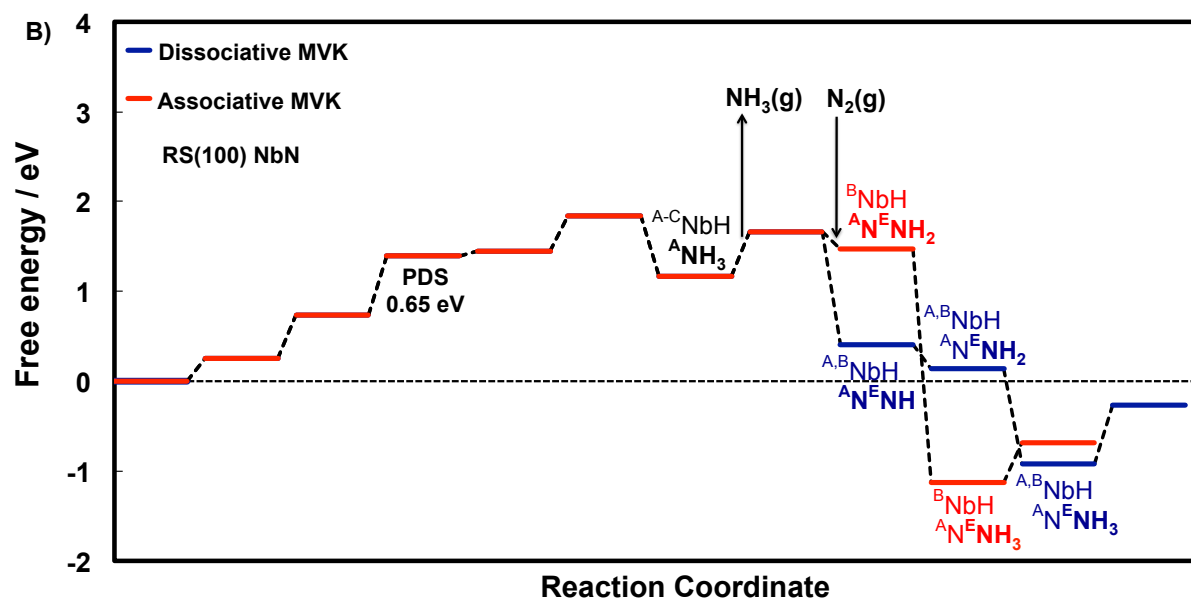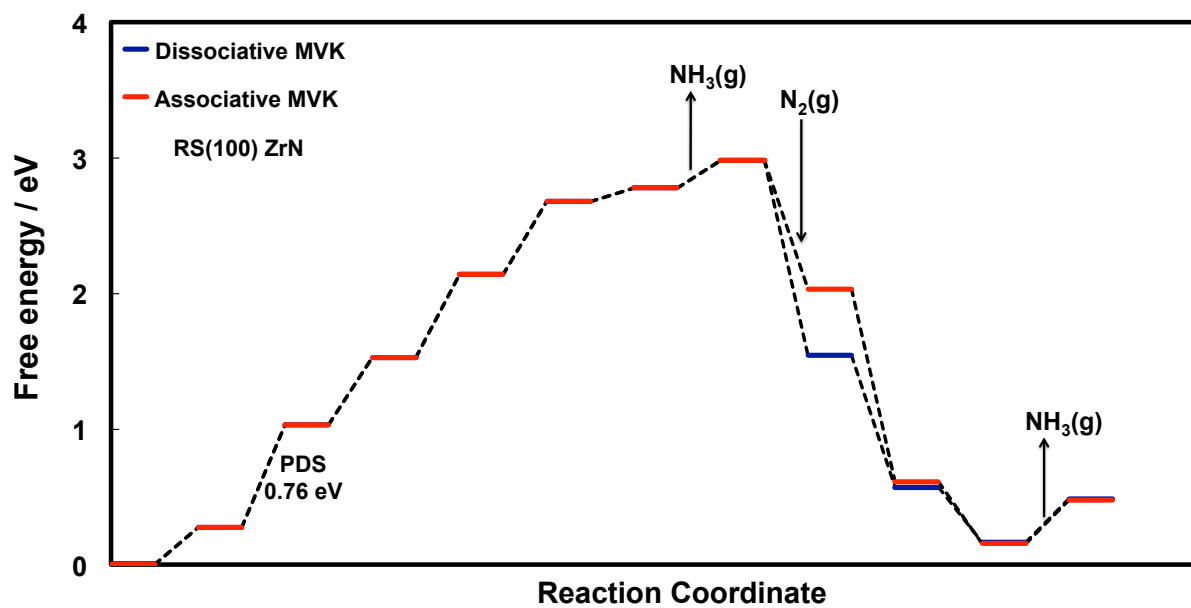
RS (100)	TS	ZPE
NH_3	0.74	0.89
H_2	0.41	0.27
N_2	0.60	0.15
*N_2	0.09	0.17
*H_{on-M}	0.03	0.14
*H_{on-N}	0.04	0.25
*2H	0.07	0.69
*3H	0.17	1.00
*N	0.04	0.08
*NH	0.06	0.34
*NH_2	0.07	0.69
*NH_3	0.18	0.99

RS (111)	TS	ZPE
NH$_3$	0.74	0.89
H$_2$	0.41	0.27
N$_2$	0.6	0.15
*N$_2$	0.03	0.20
*H	0.007	0.29
*2H	0.042	0.59
*3H	0.13	0.89
*N	0.03	0.10
*NH	0.037	0.39
*NH$_2$	0.068	0.69
*NH$_3$	0.13	0.99

ZB (100)	TS	ZPE
NH$_3$	0.74	0.89
H$_2$	0.41	0.27
N$_2$	0.60	0.15
*N$_2$	0.03	0.20
*H	0.015	0.27
*2H	0.038	0.61
*3H	0.189	0.93
*N	0.037	0.09
*NH	0.055	0.37
*NH$_2$	0.075	0.70
*NH$_3$	0.152	1.02

ZB (110)	TS	ZPE
NH$_3$	0.74	0.89
H$_2$	0.41	0.27
N$_2$	0.6	0.15
*N$_2$	0.12	0.16
*H$_{on-M}$	0.01	0.21
*H$_{on-N}$	0.007	0.29
*2H	0.013	0.64
*3H	0.05	0.96
*N	0.07	0.08

The values for adsorbed species are obtained from DFT calculations of vibrational normal modes. The gas phase values are taken from standard molecular tables.[1] Accordingly, the free energy diagrams are constructed and shown for the overall mechanisms of 2NH$_3$ formation on different facets of ZrN, NbN, CrN and VN in Figure S1.

Top panel (RS(111) ZrN):
- Legend: Dissociative MVK (blue), Associative MVK (red)
- RS(111) ZrN
- Free energy / eV (y-axis, range -1 to 7)
- Reaction Coordinate (x-axis)
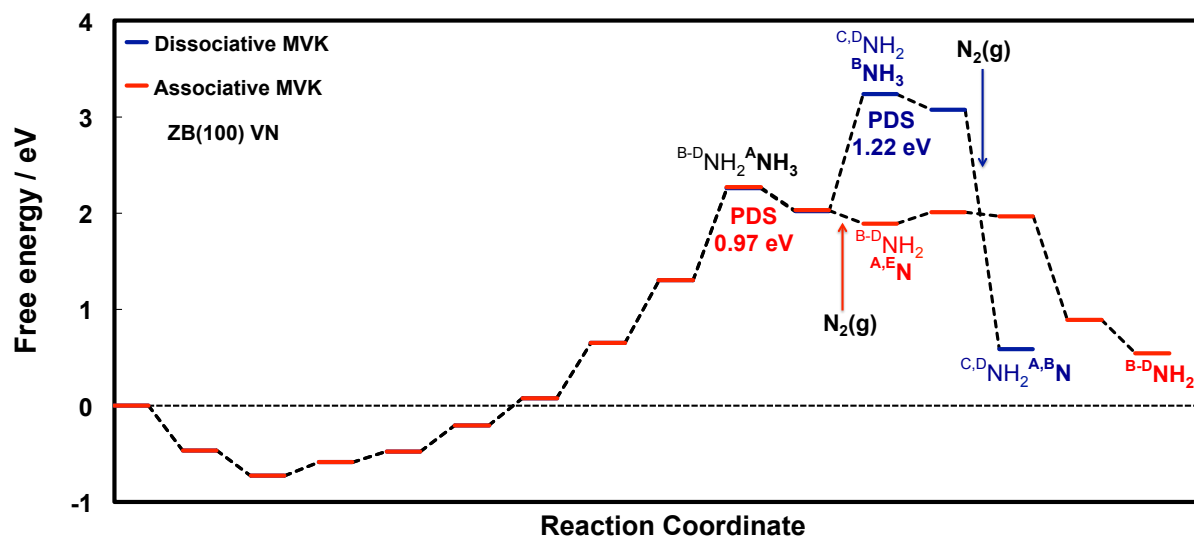- Labels: $^{C,D}NH^{B}NH_2$ $^{A}NH_3$, PDS 1.42 eV, $NH_3(g)$, $N_2(g)$, $^{C,D}NH^{B}NH_2$ $^{A,E}N$, ^{D}NH $^{B,C}NH_2$, $^{B-D}NH_2$, $^{C,D}NH_2$ $^{B}NH_3$, PDS 1.56 eV, ^{E}NH, $^{E}NH_2$, $N_2(g)$, $^{C,D}NH_2$ $^{A,B}N$, $^{E}NH_3$, $^{C,D}NH$ $^{B}NH_2$ ^{A}N

Bottom panel (RS(111) NbN):
- Legend: Dissociative MVK (blue), Associative MVK (red)
- RS(111) NbN
- Free energy / eV (y-axis, range -1 to 4)
- Reaction Coordinate (x-axis)
- Labels: PDS 1.12 eV, ^{B-D}NH $^{B}NH_2$ $^{A}NH_3$, $NH_3(g)$, $^{C,D}NH$ $^{B}NH_3$, ^{B-D}NH $^{B}NH_2$ $^{A,E}N$, $N_2(g)$, RDS 0.58 eV, $N_2(g)$, ^{B-D}NH $^{B}NH_2$ ^{A}N, $^{C,D}NH$ $^{A,B}N$

ZB(110) ZrN

PDS 1.02 eV

^{A-D}ZrH T₂ ^{B-D}NH ^ANH₂

NH₃(g)

N₂(g)

^AZrH₂ _BNH₃

^AZrH₂ _{A,E}N

N₂(g)

^AZrH₂ _{A,B}N

^AZrH₂^AN
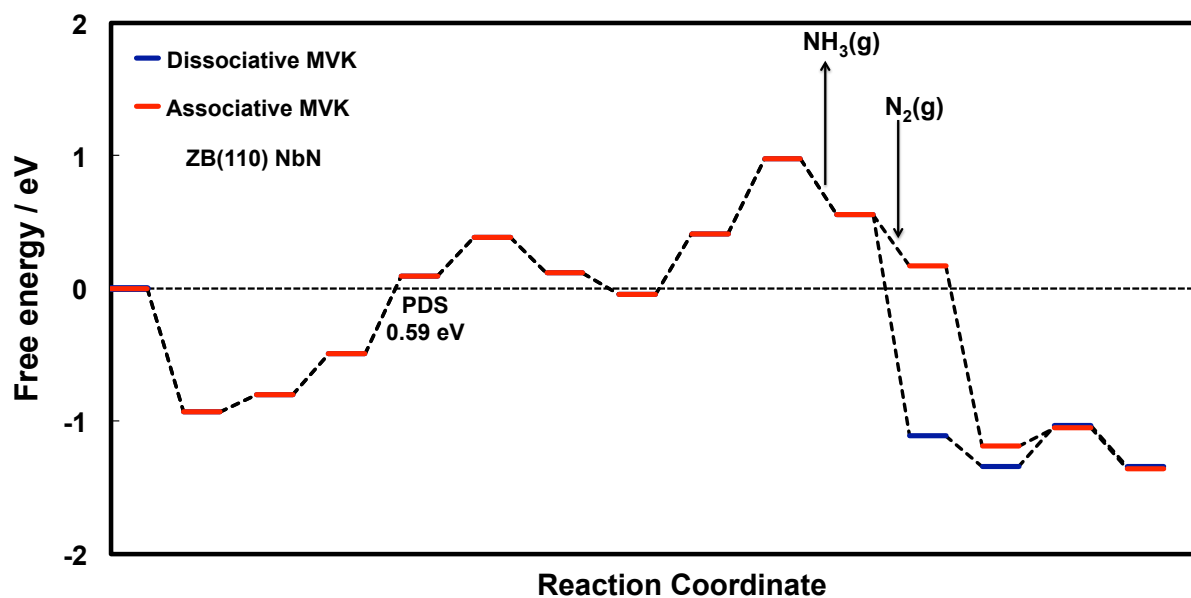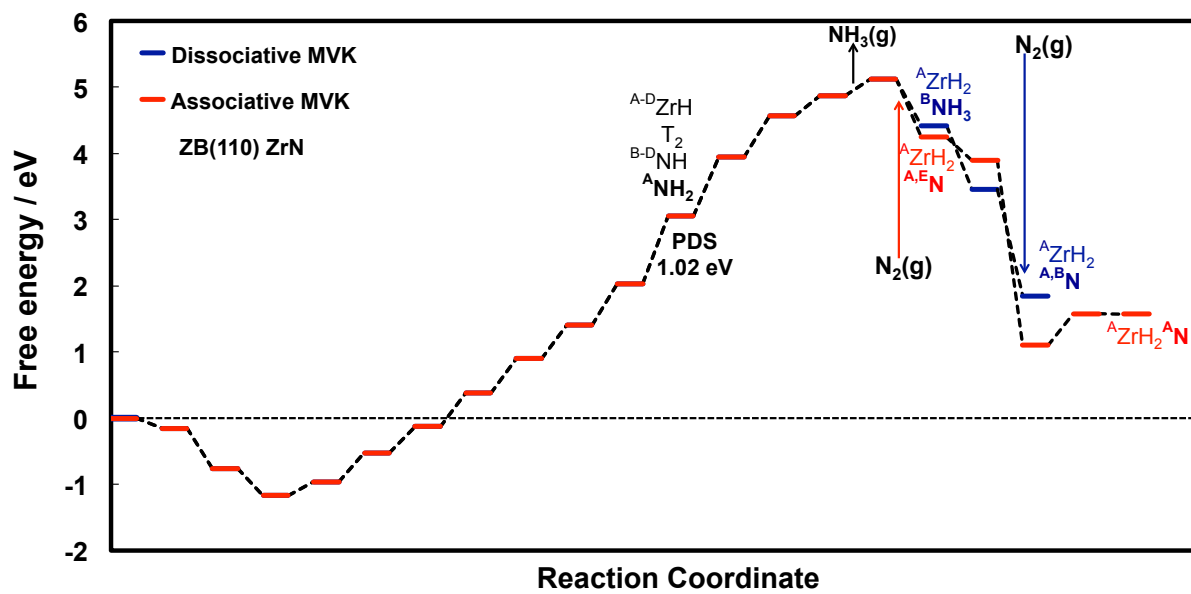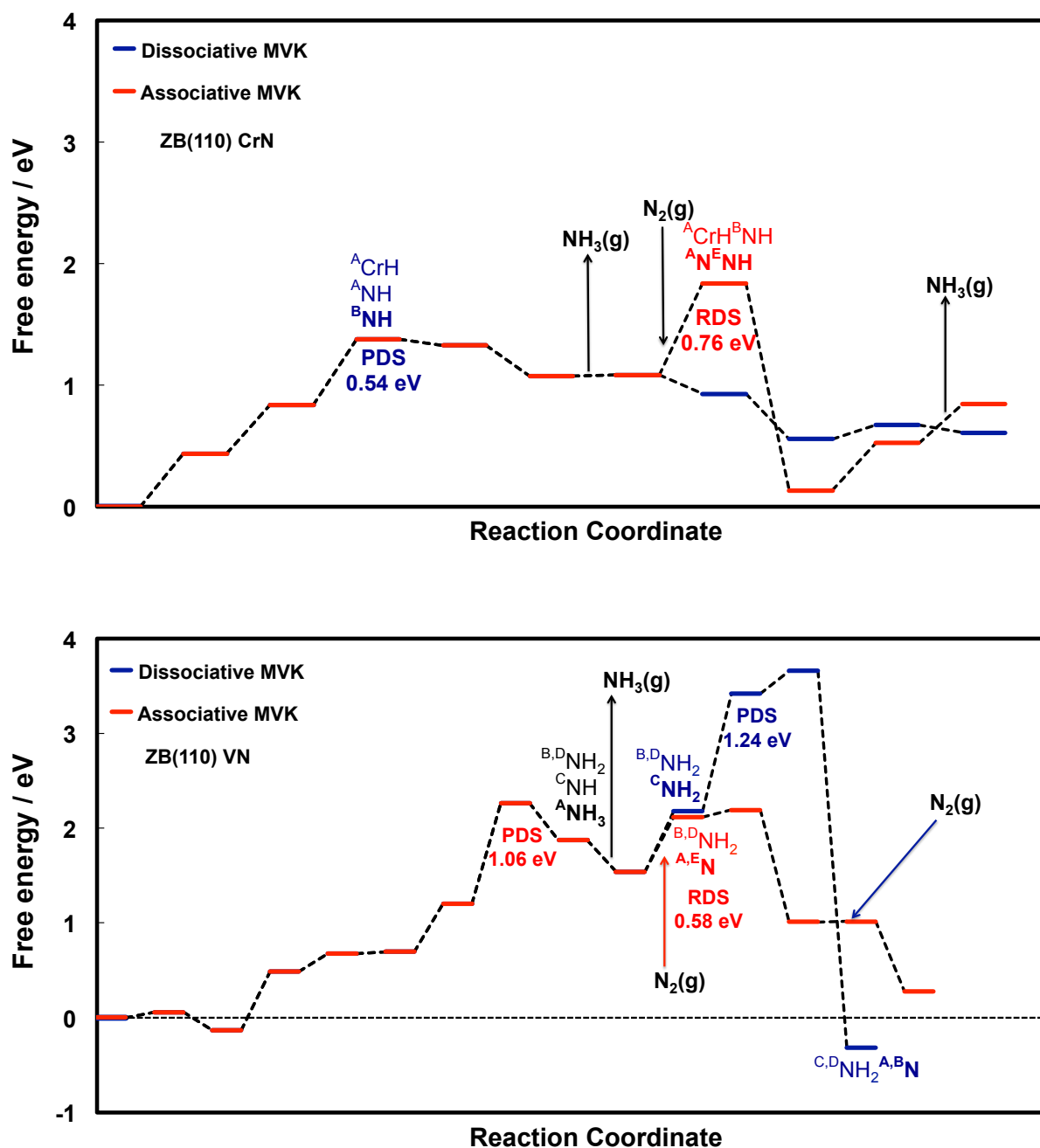
ZB(110) NbN

PDS 0.59 eV

NH₃(g)

N₂(g)

Figure S1. The free energy diagrams constructed at zero potential when vacancy is filled with $N_{2(g)}$ either associatively (red) or dissociatively (blue). The different species formed at each mechanism is shown with the relevant colour code. The labels written bold are the species formed/remained at that step. If the step with the largest free energy is an electrochemical step including proton-electron transfer, it will be tuneable by external bias and therefore called potential determining step (PDS). If the step does not include proton-electron transfer, it will not be tuned by external bias and therefore called rate-determining step (RDS).

Table S2. Energy per metal-nitrogen pair (in eV) of the various metal nitride slabs. The energies are relative to the most stable facet for each nitride. Slabs that were found to be unstable upon relaxation are denoted with a hyphen. Data taken from Ref. 2.

Nitride	RS(100)	RS(111)	ZB(100)	ZB(110)
ScN	**0.00**	0.78	1.14	0.63
TiN	**0.00**	0.32	0.94	0.84
VN	**0.00**	0.26	0.67	0.57
CrN	**0.00**	0.64	0.33	0.17
MnN	**0.00**	0.06	0.08	0.03
FeN	-	0.48	0.14	**0.00**
CoN	-	0.25	0.16	**0.00**
NiN	0.20	0.34	0.16	**0.00**
CuN	**0.00**	0.21	0.18	0.08
YN	**0.00**	0.85	1.23	0.79
ZrN	**0.00**	0.18	0.91	1.03
NbN	**0.00**	0.13	0.87	0.84
MoN	**0.00**	0.14	0.44	0.24
RuN	-	-	0.05	**0.00**
RhN	-	-	0.17	**0.00**
PdN	-	-	0.06	**0.00**
AgN	**0.00**	0.08	0.37	0.75
HfN	**0.00**	0.09	0.96	0.69
TaN	**0.00**	0.01	0.66	0.65
WN	-	-	-	-
ReN	-	-	-	-
OsN	-	-	0.05	**0.00**
IrN	-	-	0.17	**0.00**
PtN	-	-	-	-
AuN	**0.00**	-	0.09	-

To investigate the stability of the N-vacancy against poisoning by O, OH or a proton from the electrochemical media, the free energies are calculated at the onset potential proposed for the ammonia formation. The free energy of adsorption of *X (X= O or OH or H) is calculated at the onset as well as the free energy of adsorption of nitrogen (*2N). The addition of the onset potential neU to G(*2N) and to G(*X) does not cancel out when calculating dG(*2N-*X). That is because we considered adsorption of H or O or OH being affected by the value of the potential but not the adsorption of N. These results are as expected as when the bias is tuned towards more negative values, the electropositive O species bind weaker on the surface compared to H_2O, as they would rather form bonds with the surface when the bias is more positive:

$$H_2O + * \longrightarrow *O + 2H^+ + 2e^-$$

Conversely, the H adsorption free energy becomes more negative when the bias is lowered:

$$H^+ + e^- \longrightarrow *H$$
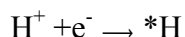
While analysing different mechanisms for reduction of nitrogen to ammonia, we found that the Mars-van Krevelen mechanism is more energetically favourable on the surface of nitrides compared to the common associative or dissociative mechanisms. For the associative mechanism, the formation of *N_2H was found to be thermodynamically unfavored on the surface of these nitrides. For the dissociative mechanism, very large kinetic barriers of more than 2.5 eV were found for splitting of di-nitrogen on the surface. The

results of these two mechanisms are shown below. For ammonia formation via associative mechanism on the clean surface of RS(111) and ZB(100), there was no stable site found on the surface for adsorption of di-nitrogen. Via dissociative mechanism as well, no stable adsorption site was found on the surface of the RS(111) and ZB(100) for addition of the second *N. On the surface of the ZB(110), large surface reconstructions were observed upon addition of the second *N and therefore those facets are not included here.
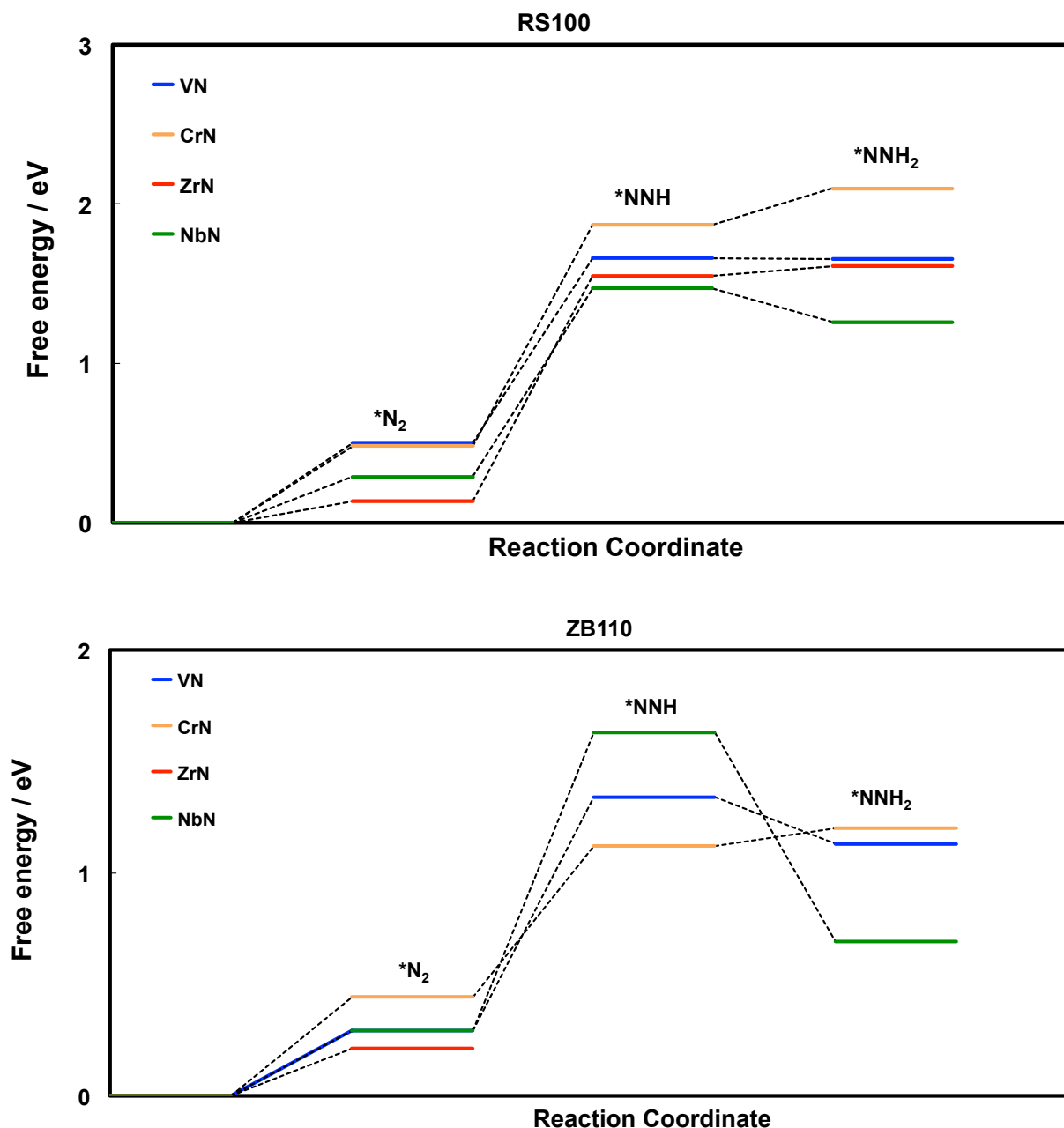
Figure S2. The first three elementary steps in the free energy diagram towards NH_3 formation via an associative mechanism on the clean surface of the nitrides. The N_2 adsorption on the surface is endothermic in most cases and the first protonation step of the adsorbed N_2 is endergonic making this mechanism unlikely to occur at ambient conditions. On the surface of the RS(111) and ZB(100) facets of these nitrides, no stable adsorption site was found for adsorption of di-nitrogen. On the ZB(110) of ZrN, *NNH formation led to large reconstruction of the surface and therefore, the *NNH step is not shown here.
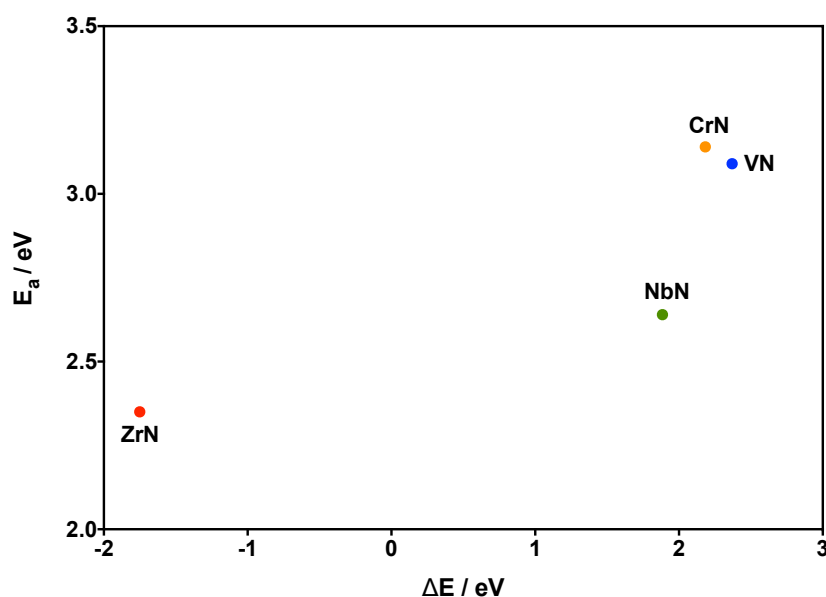
Figure S3. Activation energy (Ea, in eV) and reaction energy (ΔE, in eV) of N_2 dissociation on the clean surface of the RS(100) facet of the most promising metal nitrides. For all nitrides, there is a very large energy barrier for splitting of dinitrogen on the surface making the dissociative mechanism very unlikely to occur at ambient conditions. No stable adsorption site was found on the surface of the RS(111) and ZB(100) for addition of the second *N. On the surface of the ZB(110), large surface reconstructions were observed upon addition of the second *N and therefore those facets are not included here.

References

1. Atkins, W. *Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, 1998; pp 485, 866–867, 925–927 and 942.

2. Abghoui, Y.; Garden, A. L.; Hlynsson, V. F.; Björgvinsdóttir, S.; Ólafsdóttir, H.; Skúlason, E. *Phys. Chem. Chem. Phys.* **2015**, 17, 4909–4918.