Theoretical insights into the electroreduction of nitrate to ammonia on the graphene-based single-atom catalyst

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Supporting Information

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Table S1 Zero-point energy corrections (ΔE_{ZPE}) and entropic contributions ($T\Delta S$) (at 298.15 K) to the free energies of the key intermediates.

Species	ΔE_{ZPE} (eV)	$T\Delta S$ (eV)
NO_3*	0.42	0.23
NO_3H*	0.61	0.33
NO_2*	0.27	0.20
HNO_2*	0.55	0.20
NO_2H*	0.55	0.20
HNO_2H*	0.84	0.34
NO*-end	0.19	0.09
NO*-side	0.16	0.14
HNO*-end	0.47	0.18
HNO*-side	0.46	0.15
HNOH*	0.78	0.17
NH*	0.32	0.12
NH_2*	0.68	0.10
NO_2*+OH*	0.64	0.29
NO*+OH*	0.54	0.25
HNO*+OH*	0.85	0.23
H_2NO*+OH*	1.17	0.30
O*+OH*	0.44	0.15
H_2NO*	0.78	0.20
H_2NOH*	1.13	0.22
H_2N*+OH*	1.05	0.18
O*	0.06	0.11
OH*	0.34	0.13

Table S2 Zero-point energy corrections (ΔE_{ZPE}) and entropic contributions ($T\Delta S$) (at 298.15 K) to the free energies of the relevant molecules, and their free energy correction ($\Delta G_{correct}$) referenced to the experimental formation energy.

Species	ΔE_{ZPE} (eV)	$T\Delta S$ (eV)	$\Delta G_{correct}$ (eV)
HNO_3(g)	0.70	0.83	1.06
HNO_2 trans(g)	0.53	0.77	0.67
NO_2(g)	0.23	0.74	0.93
NH_3(g)	0.89	0.60	0.18
H_2(g)	0.27	0.40	--
H_2O(g)	0.56	0.67	--

Table S3 The key parameters of the TMN_3@G and TMN_4@G systems. Average distance (d_{TM-N}) between the embedded TM atom and its bonded N atoms, binding energy (E_b) of the TM atom with respect to the N-doped graphene and the isolated metal atom, net charge (ΔQ) of the TM atom, spin magnetic moment (M) of the whole system (the value outside the parenthesis) and the embedded TM atom (the value inside the parenthesis).

TMN_x	d_{TM-N} (Å)	E_b (eV)	ΔQ (e)	M (μ_B)
TiN_3	1.95	-5.22	-1.74	2.19 (1.58)
VN_3	1.95	-7.05	-1.50	2.44 (2.64)
CrN_3	1.96	-3.86	-1.26	4.56 (3.87)
MnN_3	2.01	-4.10	-1.15	5.32 (4.89)
FeN_3	1.87	-4.92	-1.16	3.26 (3.29)
CoN_3	1.83	-5.21	-0.92	2.30 (2.11)
NiN_3	1.84	-4.60	-0.93	1.47 (1.26)
TiN_4	2.04	-8.24	-1.88	1.46 (1.32)
VN_4	1.98	-7.82	-1.68	2.78 (2.60)
CrN_4	1.95	-6.89	-1.55	3.99 (3.68)
MnN_4	1.92	-6.79	-1.60	3.02 (3.20)
FeN_4	1.90	-7.62	-1.32	2.00 (2.03)
CoN_4	1.88	-7.92	-1.01	0.98 (0.82)
NiN_4	1.88	-7.76	-1.01	0.00 (0.00)

Table S4 Binding free energy of NO_3^- ($\Delta G(NO_3^*)$) and H ($\Delta G(H^*)$), the net charge of the NO_3^*, and the distance between the O atoms in NO_3^* and its bonded TM atom.

TMN_x	$\Delta G(NO_3^*)$ (eV)	$\Delta G(H^*)$ (eV)	$\Delta Q(NO_3^*)$ (*e*)	*d*(M-O*) (Å)
TiN_3	-3.62	-0.65	0.86	2.12, 2.14
VN_3	-3.23	-0.45	0.82	2.06, 2.13
CrN_3	-3.44	-0.34	0.83	2.02, 2.04
MnN_3	-2.71	-0.31	0.78	2.01, 2.01
FeN_3	-2.66	0.42	0.76	1.99, 1.99
CoN_3	-2.45	0.01	0.70	1.95, 1.95
NiN_3	-2.11	0.23	0.67	1.93, 1.93
TiN_4	-3.37	-0.49	0.78	2.13, 2.14
VN_4	-2.73	-0.12	0.82	2.06, 2.06
CrN_4	-1.33	0.32	0.75	1.93
MnN_4	-0.87	0.48	0.79	2.03
FeN_4	-0.70	0.32	0.68	1.91
CoN_4	-0.55	0.12	0.66	1.94
NiN_4	0.20	1.61	0.68	2.21

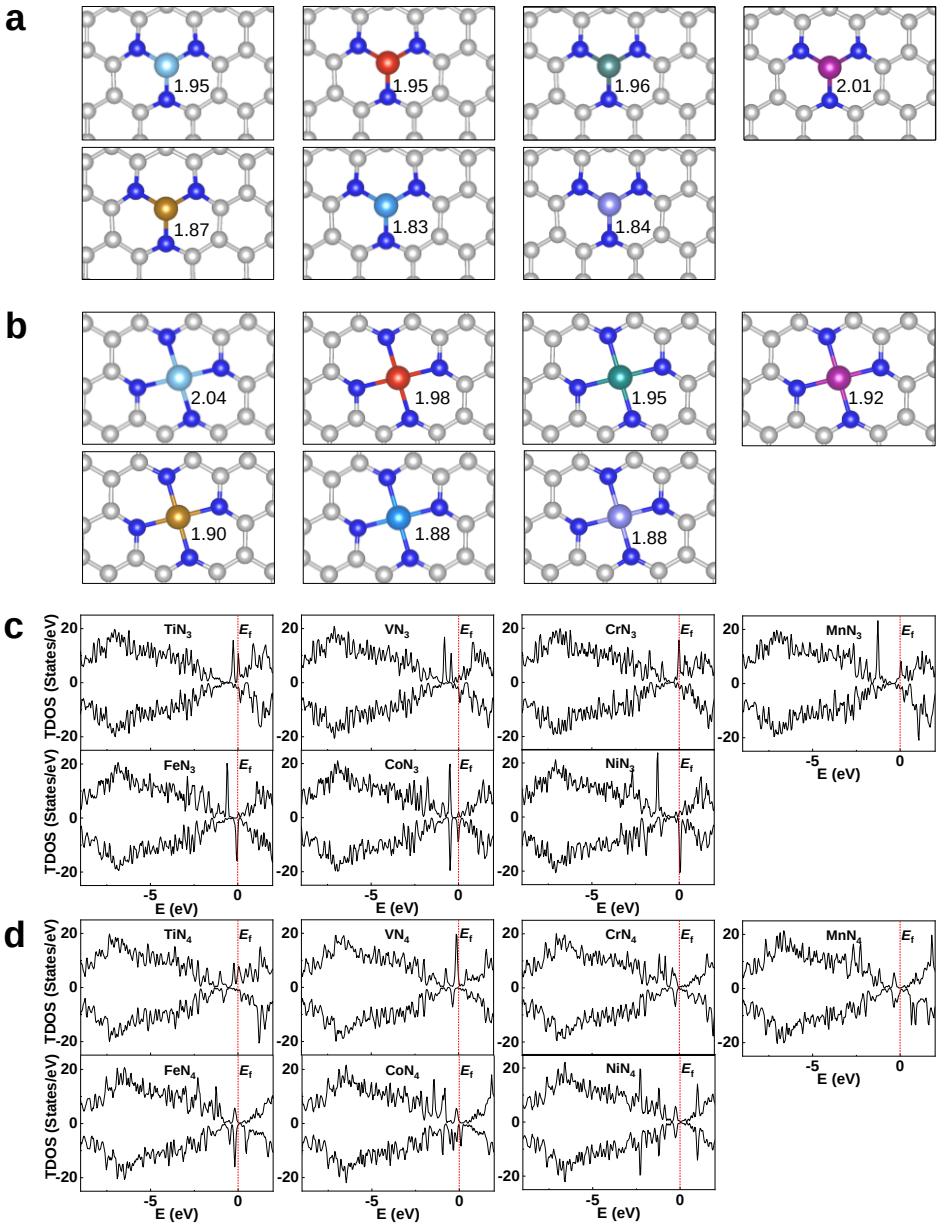

Fig. S1. The atom configurations with TM-N bond lengths (in Å) of the TMN_3@G (a) and TMN_4@G (b) systems. The total densities of states (TDOS) of the TMN_3@G (c) and TMN_4@G (d) systems. The vertical dashed line denotes the position of Fermi level (E_f). The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

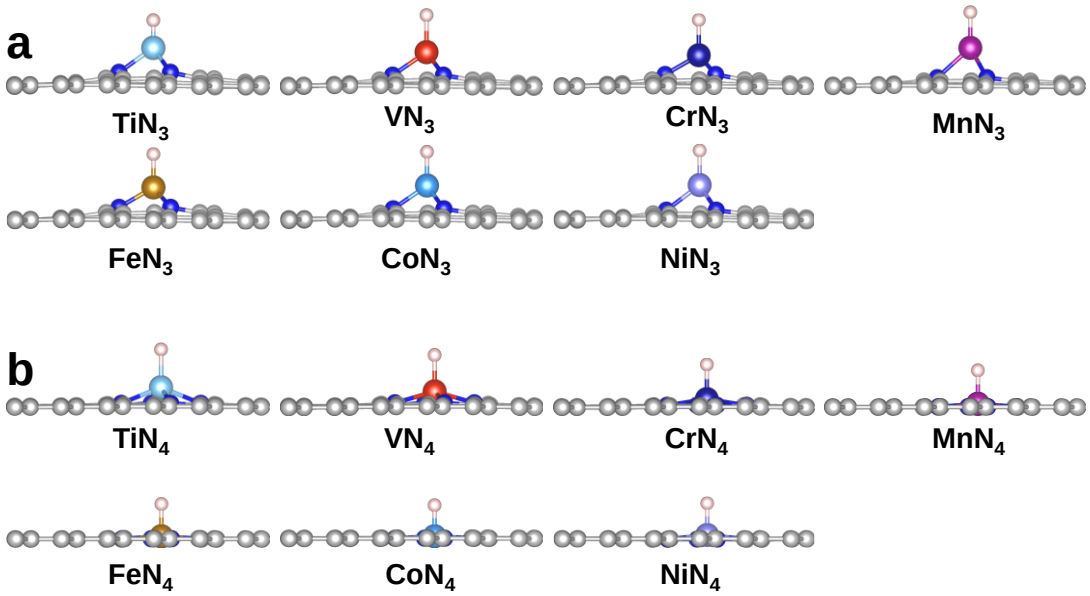

Fig. S2. The most stable adsorption configurations of H atoms on TMN_3@G (a) and TMN_4@G (b).

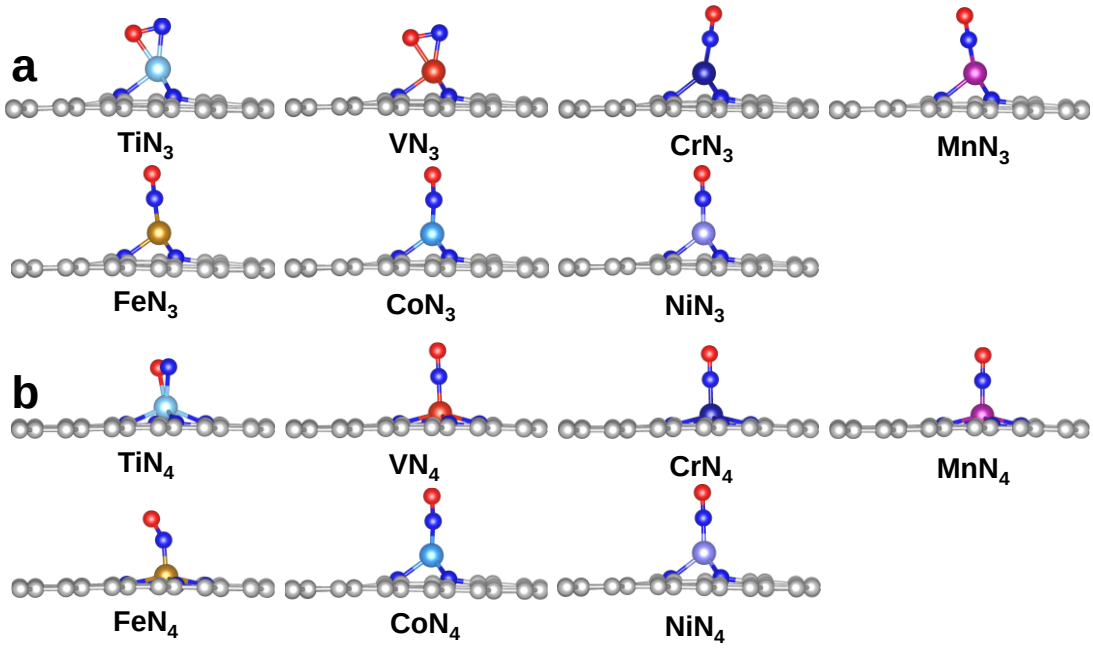

Fig. S3. The most stable adsorption configurations of NO molecules on TMN_3@G (a) and TMN_4@G (b).

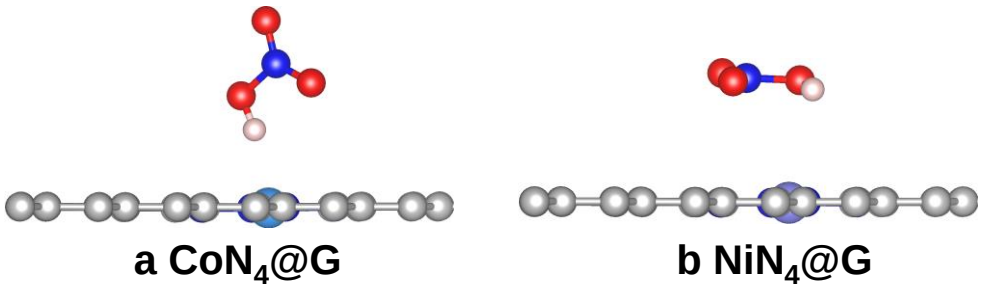

Fig. S4. The most stable configurations of HNO_3* for CoN_4@G (a) and NiN_4@G (b).

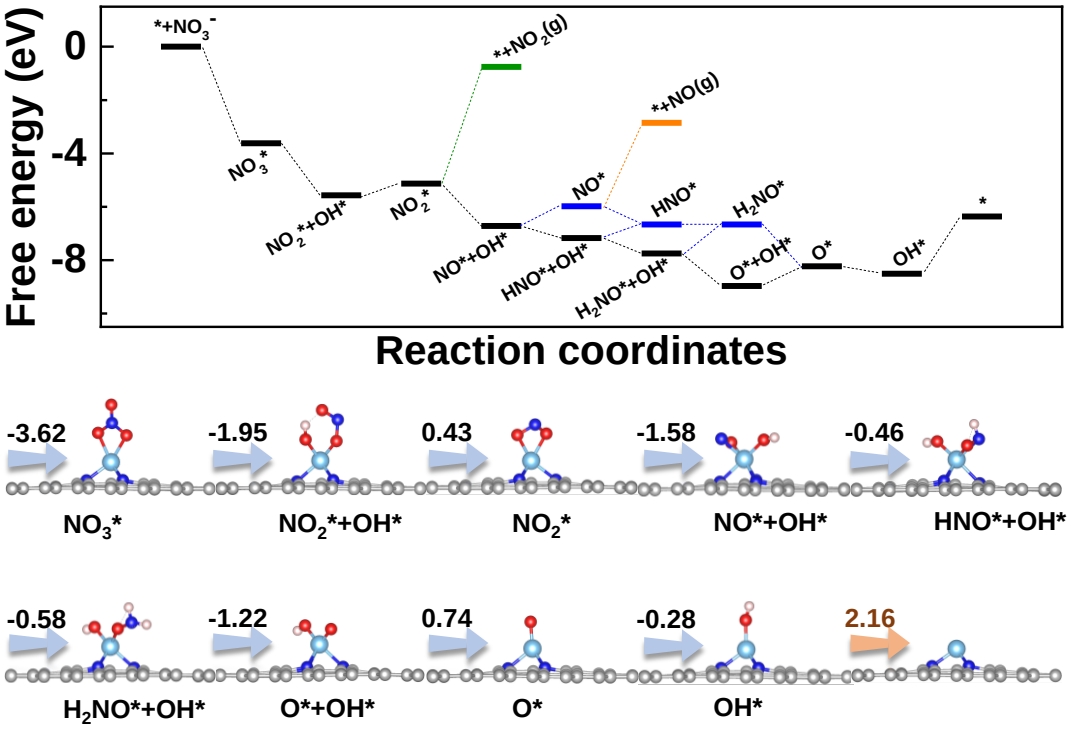

Fig. S5. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on TiN_3@G.

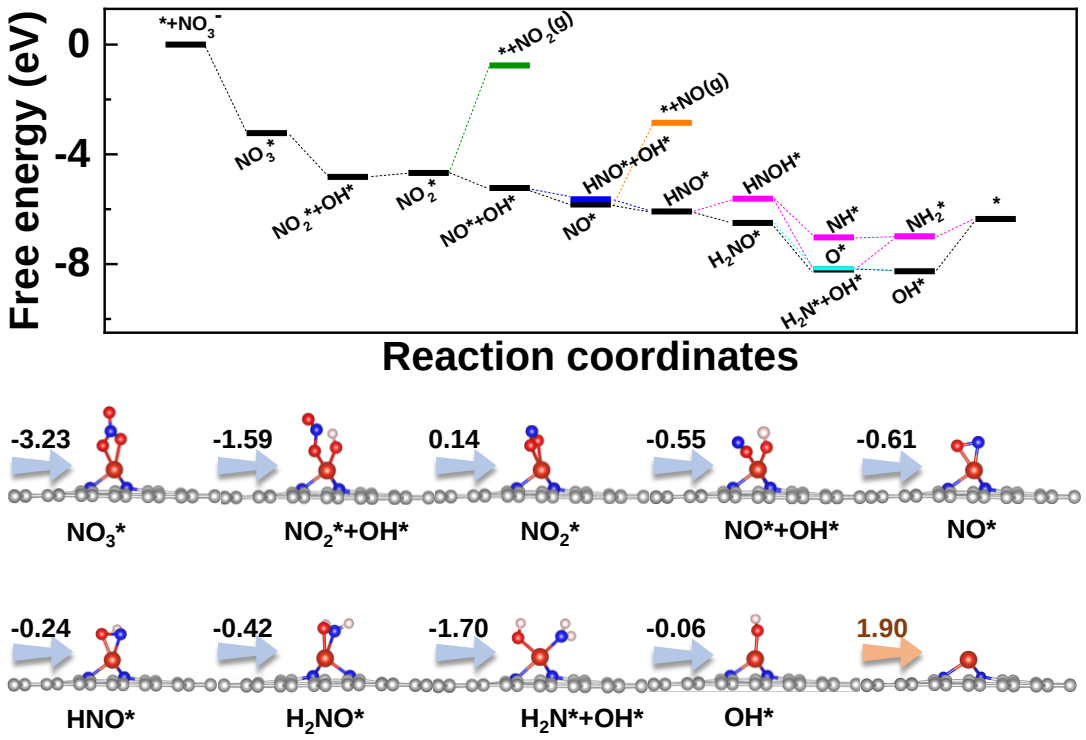

Fig. S6. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on VN_3@G.

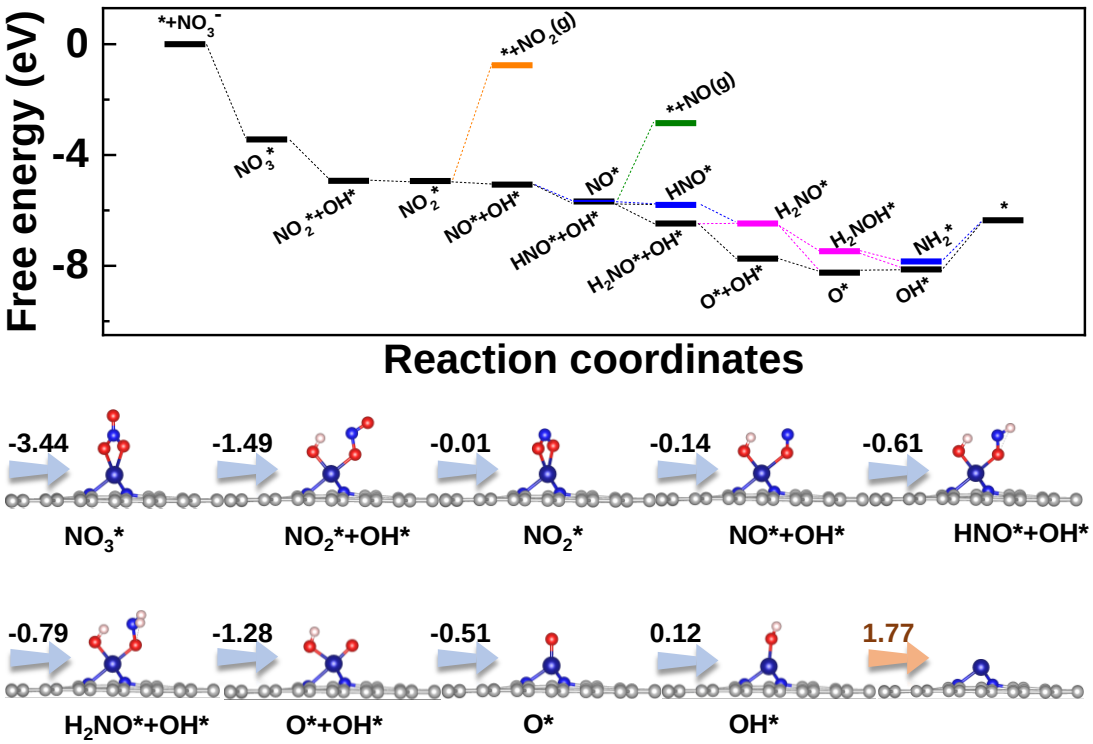

Fig. S7. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on CrN_3@G.

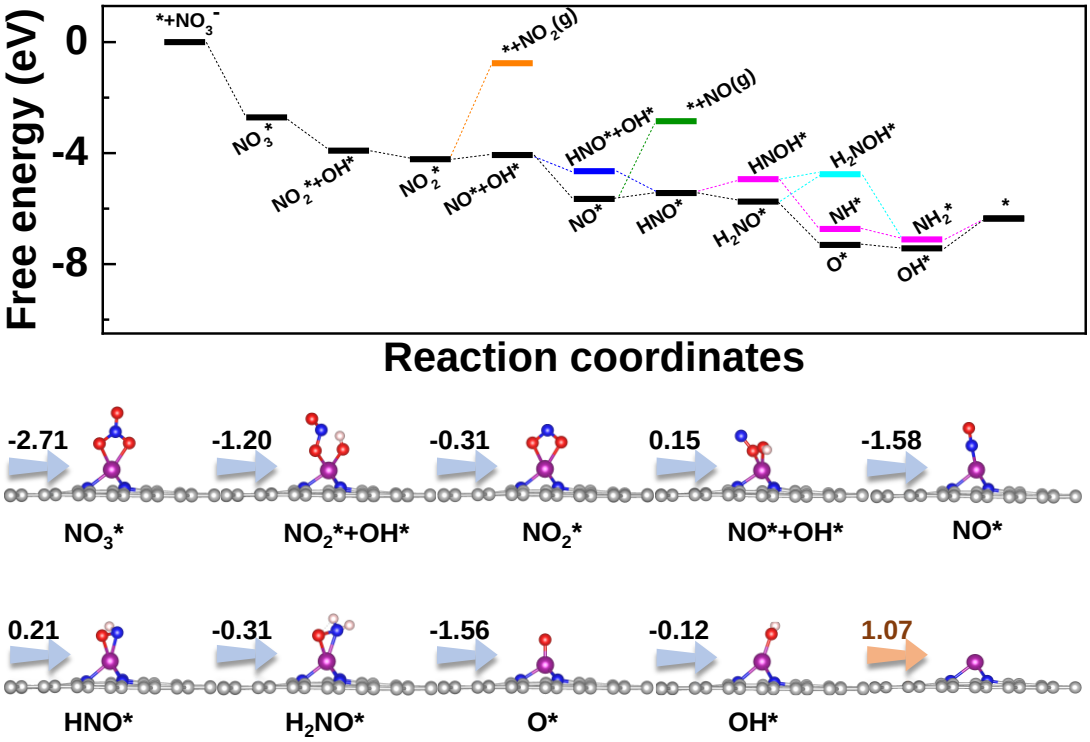

Fig. S8. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on MnN_3@G.

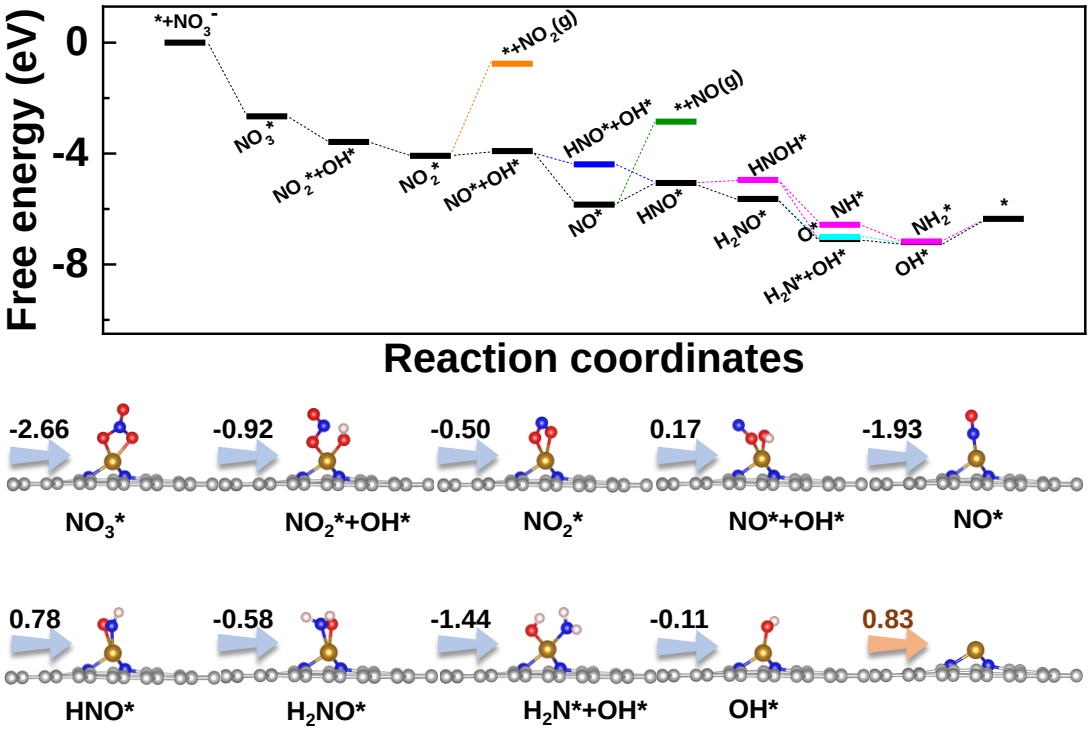

Fig. S9. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on FeN_3@G.

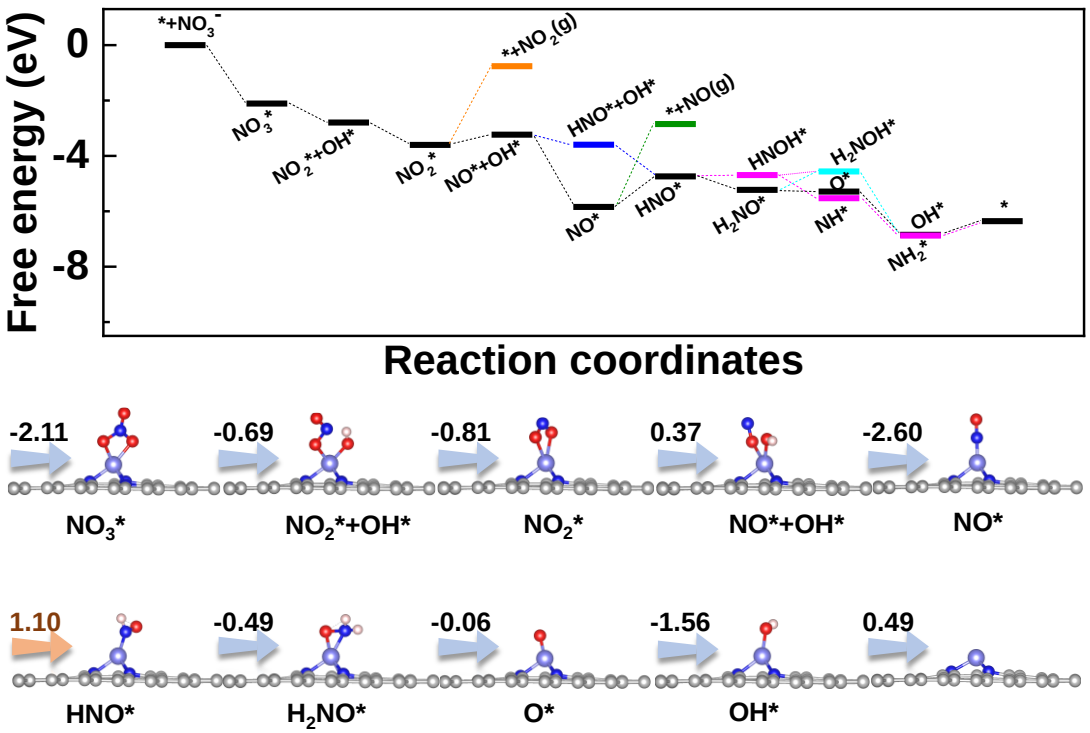

Fig. S10. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on NiN_3@G.

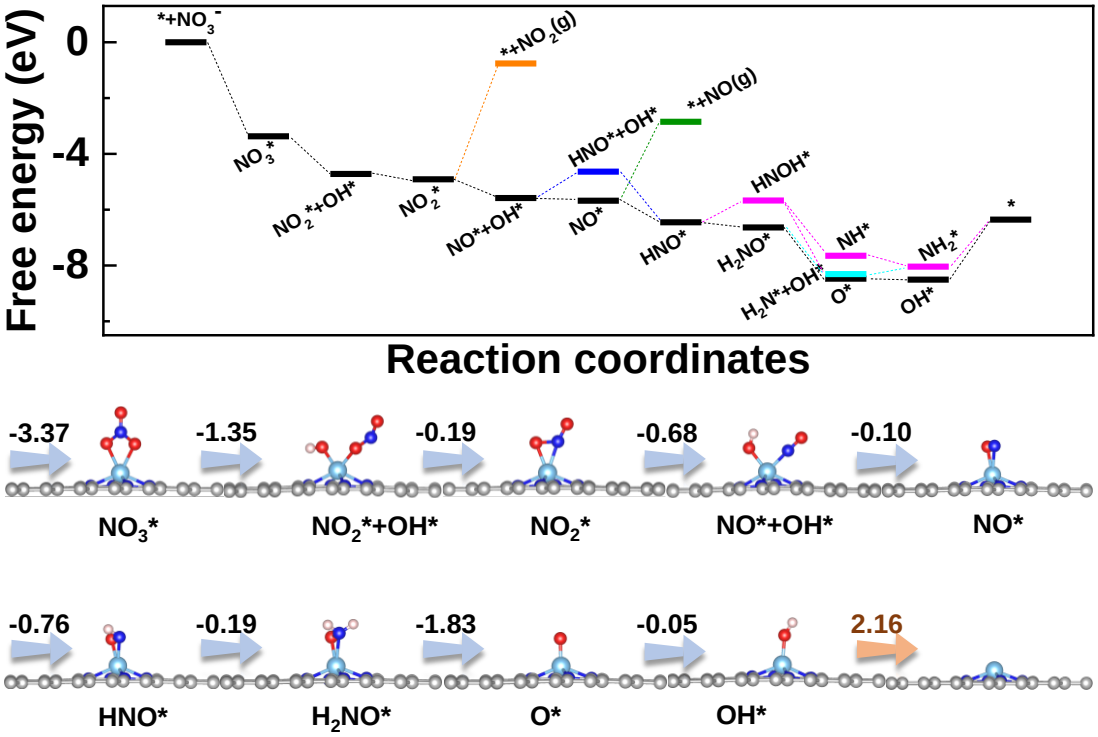

Fig. S11. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on TiN_4@G.

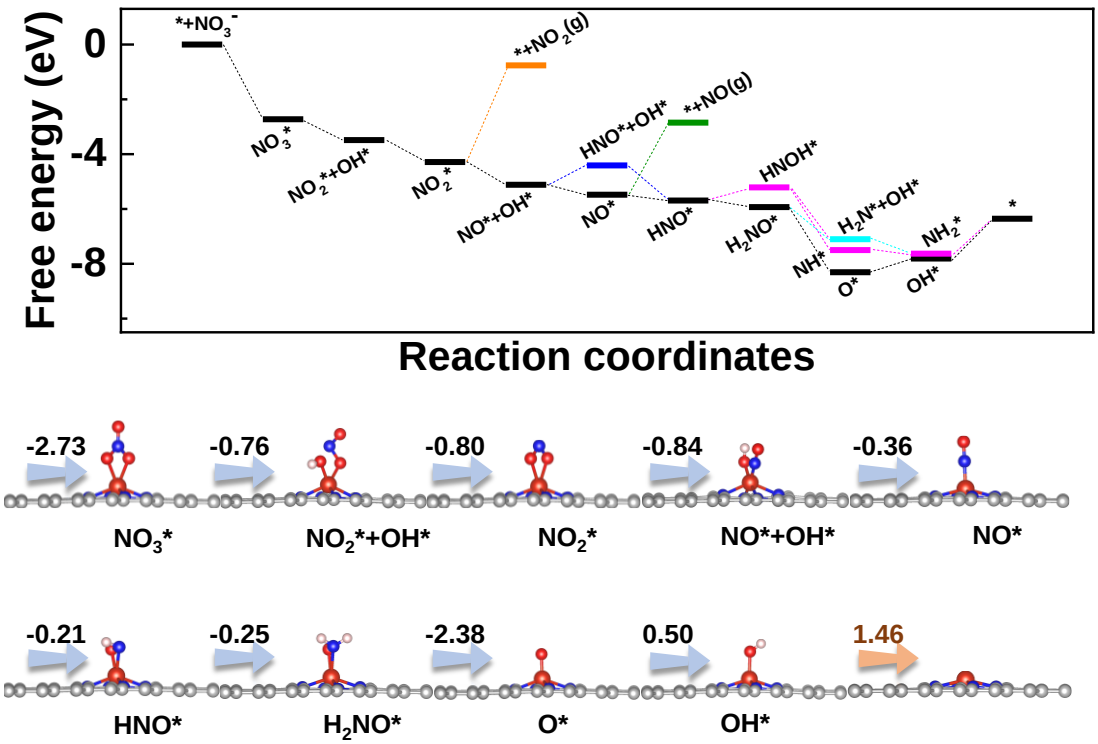

Fig. S12. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on VN_4@G.

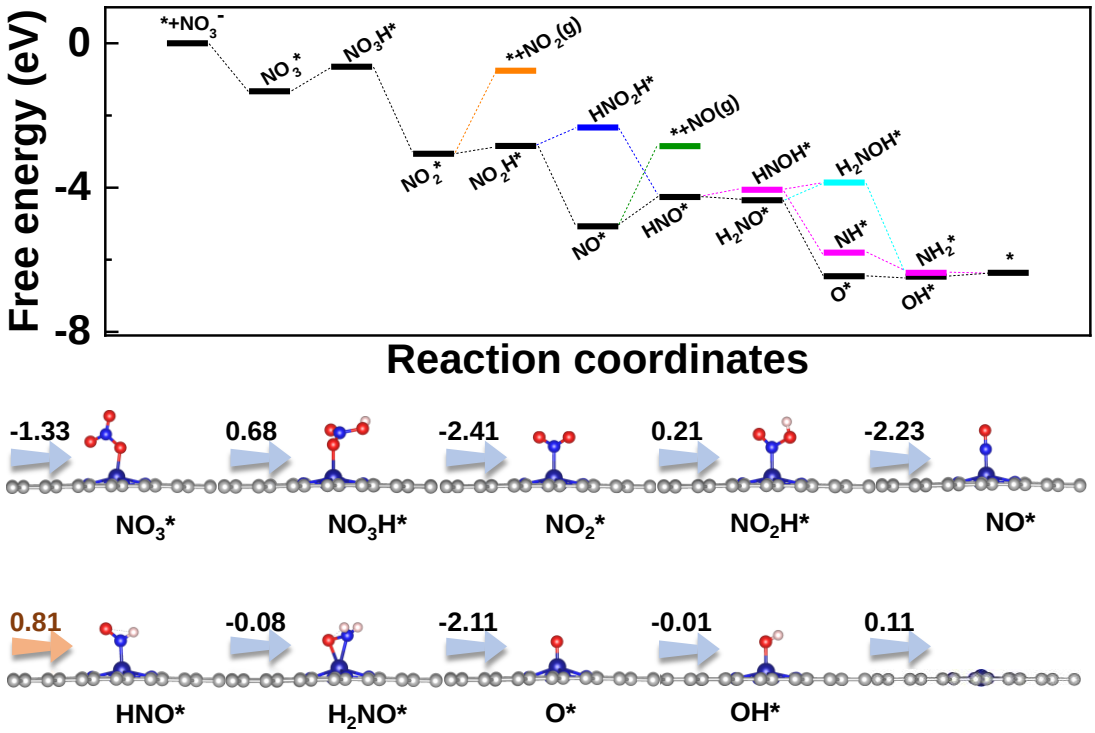

Fig. S13. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on CrN_4@G.

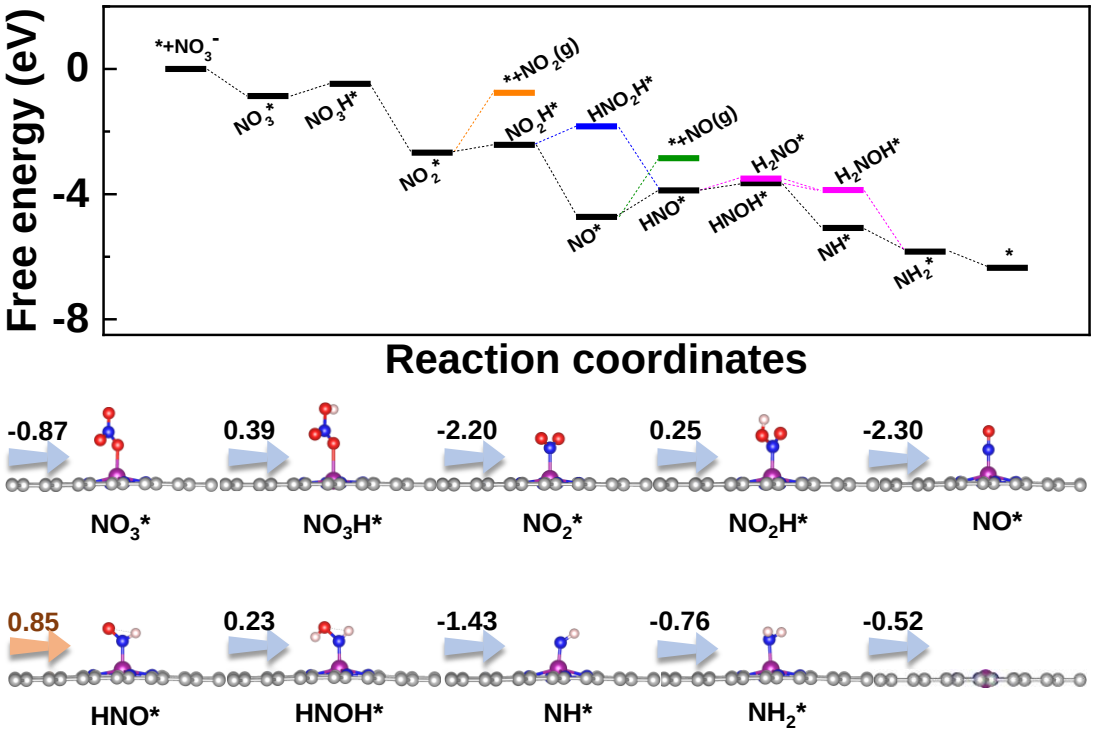

Fig. S14. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on MnN_4@G.

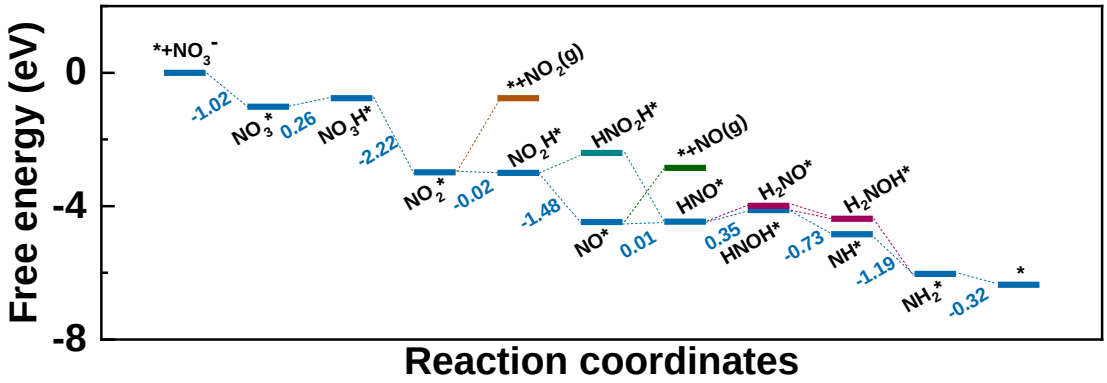

Fig. S15. Free energy diagram for the eNO_3RR on FeN_4@G with consideration of the solvation effect.

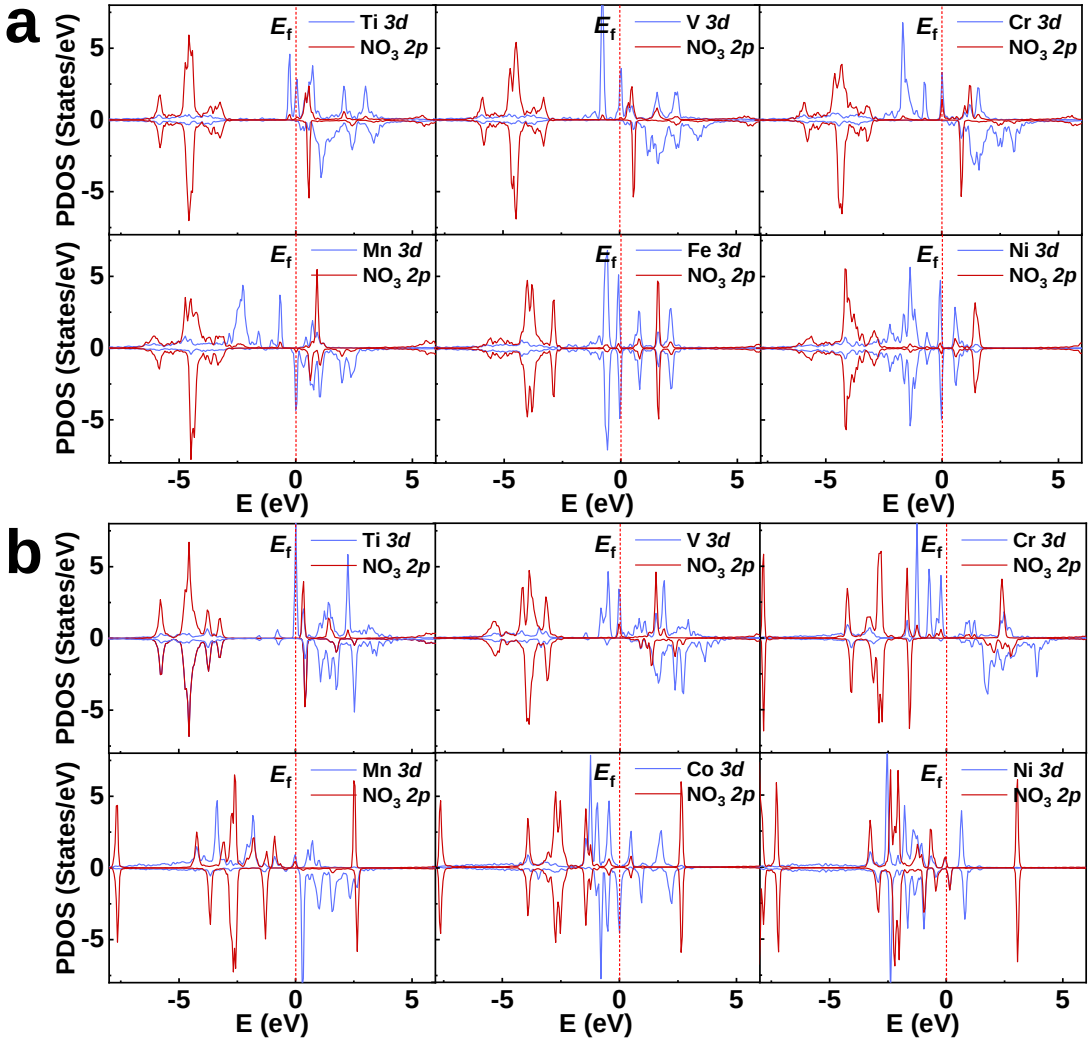

Fig. S16. Projected densities of states (PDOS) of the TM 3d states and O (in NO_3*) 2p states, which is bonded with the TM atom. (a) and (b) are for TMN_3@G and TMN_4@G, respectively. The vertical dashed line denotes the position of Fermi level (E_f). The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

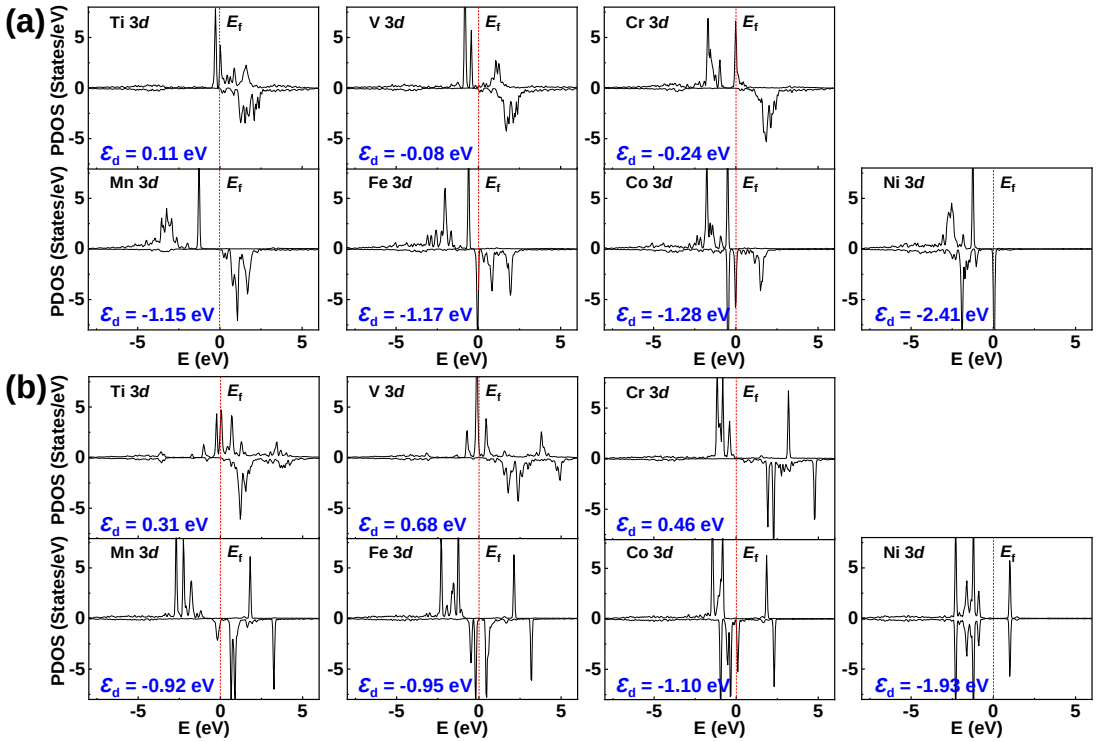

Fig. S17. Projected densities of state (PDOS) and the d-band center (ε_d) of the TM 3d states of the pristine TMN_3@G and TMN_4@G. The vertical dashed line denotes the position of Fermi level (E_f). The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

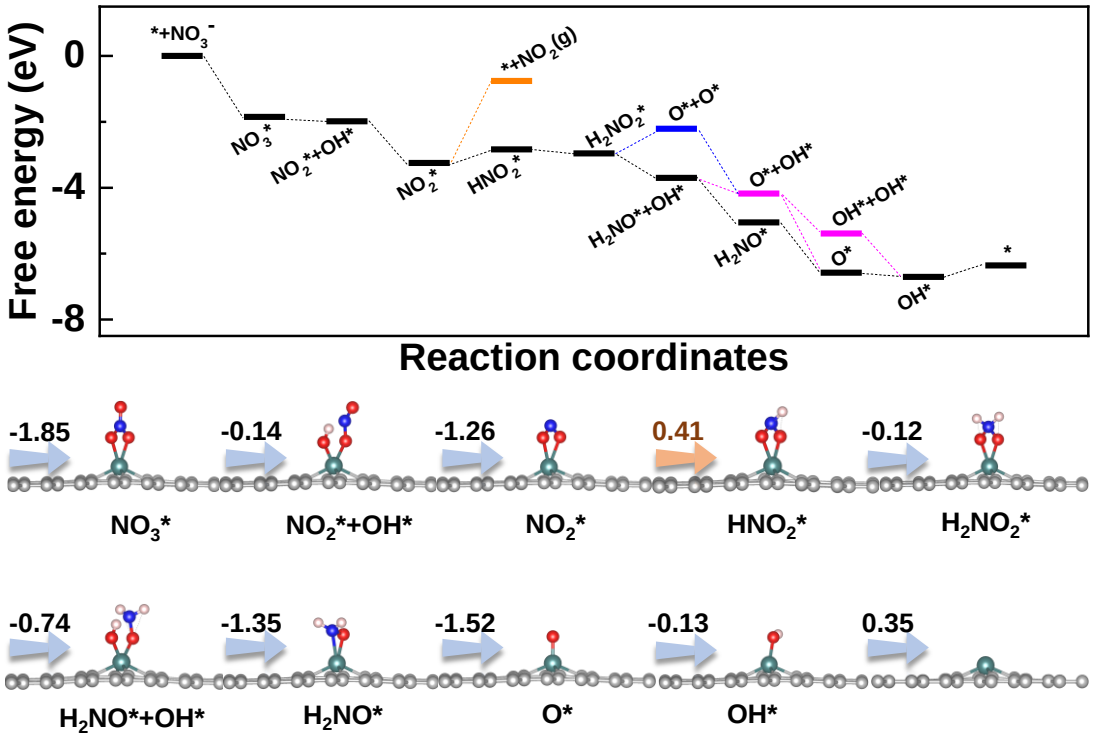

Fig. S18. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on RuC_4@G.

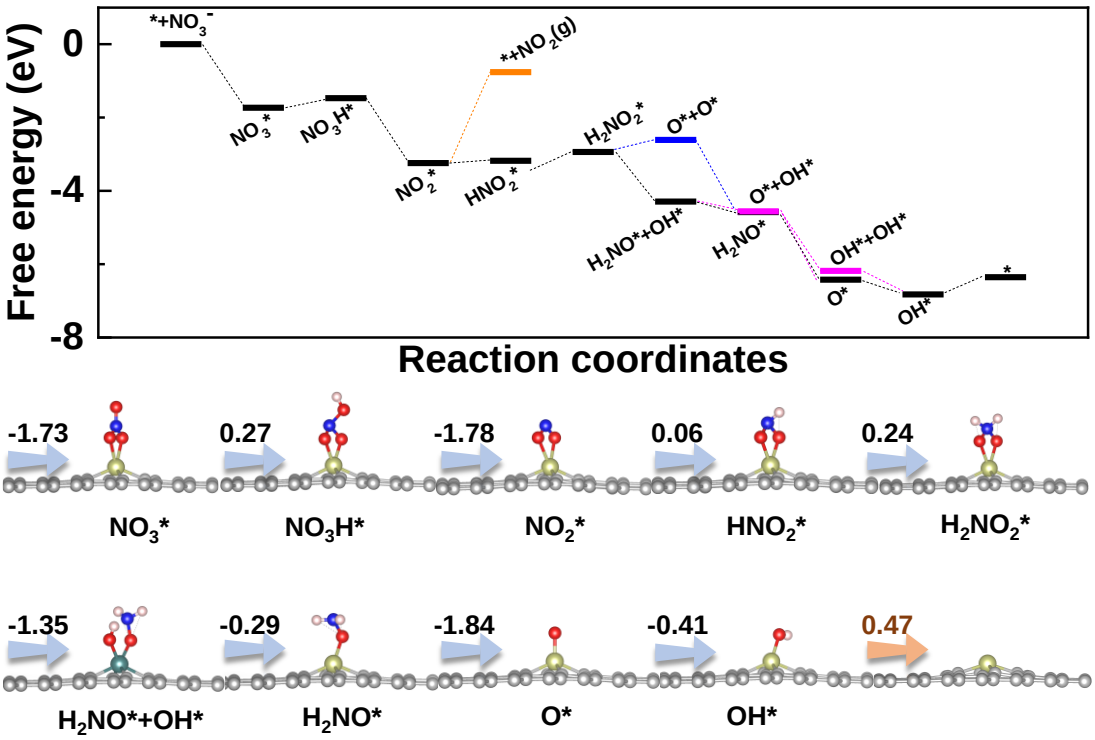

Fig. S19. Free energy diagram together with the configurations of corresponding intermediates for the eNO_3RR on IrC_4@G.