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Nitric Oxide Reduction Reaction for Efficient Ammonia Synthesis on Topological Nodal-Line Semimetal Cu_2Si Monolayer

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Table S1 Elementary reactions for all the considered pathways for NORR towards NH_3 synthesis.

End-on	
N-distal	**N-alternating**
NO (g) + * → *NO	NO (g) + * → *NO
*NO + H^+ +e^- → *HNO	*NO + H^+ +e^- → *HNO
*HNO + H^+ +e^- → *H_2NO	*HNO + H^+ +e^- → *HNOH
*H_2NO + H^+ +e^- → *H_2NOH	*HNOH + H^+ +e^- → *H_2NOH
*H_2NOH + H^+ +e^- → *NH_2 + H_2O	*H_2NOH + H^+ +e^- → *NH_2 + H_2O
*NH_2 + H^+ +e^- → *NH_3	*NH_2 + H^+ +e^- → *NH_3
O-alternating	**O-distal**
NO (g) + * → *NO	NO (g) + * → *NO
*NO + H^+ +e^- → *NOH	*NO + H^+ +e^- → *NOH
*NOH + H^+ +e^- → *HNOH	*NOH + H^+ +e^- → *N + H_2O
*HNOH + H^+ +e^- → *NH + H_2O	*N + H^+ +e^- → *NH
*NH + H^+ +e^- → *NH_2	*NH + H^+ +e^- → *NH_2
*NH_2 + H^+ +e^- → *NH_3	*NH_2 + H^+ +e^- → *NH_3
Side-on	
O-first	**O-enzymatic**
NO (g) + * → *NO	NO (g) + * → *NO
*NO + H^+ +e^- → *NOH	*NO + H^+ +e^- → *NOH
*NOH + H^+ +e^- → *N + H_2O	*NOH + H^+ +e^- → *HNOH
*N + H^+ +e^- → *NH	*HNOH + H^+ +e^- → *NH + H_2O
*NH + H^+ +e^- → *NH_2	*NH + H^+ +e^- → *NH_2
*NH_2 + H^+ +e^- → *NH_3	*NH_2 + H^+ +e^- → *NH_3
N-enzymatic	**N-first**
NO (g) + * → *NO	NO (g) + * → *NO
*NO + H^+ +e^- → *HNO	*NO + H^+ +e^- → *HNO
*HNO + H^+ +e^- → *HNOH	*HNO + H^+ +e^- → *H_2NO
*HNOH + H^+ +e^- → *H_2NOH	*H_2NO + H^+ +e^- → *O + NH_3
*H_2NOH + H^+ +e^- → *NH_2 + H_2O	*O + H^+ +e^- → *OH
*NH_2 + H^+ +e^- → *NH_3	*OH + H^+ +e^- → *H_2O

Table S2 Computed total energies (E), zero-point energies (E_{ZPE}) and entropy (TS) of NORR intermediates on Cu–Si-bridge site with N-end configuration of NO adsorption.

	E (eV)	E_{ZPE} (eV)	TS (eV)	G (eV)
*NO	–121.20	0.18	0.13	–121.15
*NOH	–124.85	0.47	0.15	–124.52
*HNOH	–129.41	0.75	0.18	–128.84
*NH	–119.79	0.38	0.04	–119.45
*NH_2	–124.42	0.72	0.07	–123.77
*NH_3	–128.41	1.03	0.15	–127.53

Table S3 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on Cu–Si-bridge site with NO-side configuration of NO adsorption.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NO	–120.57	0.16	0.11	–120.52
*HNO	–125.27	0.47	0.13	–124.89
*H_2NO	–129.99	0.84	0.14	–129.29
*HNOH	–128.53	0.78	0.15	–127.89
*O	–114.78	0.07	0.06	–114.77
*H_2NOH	–132.76	1.09	0.26	–131.92
*NH	–119.79	0.38	0.04	–119.45
*OH	–119.40	0.34	0.14	–119.20
*H_2O	–122.49	0.65	0.17	–122.02

Table S4 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on Si site with N-end configuration of NO adsorption.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NO	–121.04	0.17	0.18	–121.04
*HNO	–125.15	0.47	0.21	–124.89
*HNOH	–129.31	0.78	0.22	–128.75
*H_2NOH	–133.52	1.13	0.21	–132.60
*NH_2	–124.36	0.65	0.16	–123.86
*NH_3	–128.41	1.03	0.15	–127.53

Table S5 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on Si site with N-end configuration of NO adsorption by DFT + *U* method.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NO	–96.82	0.18	0.16	–96.80
*HNO	–100.85	0.47	0.20	–100.58
*HNOH	–104.94	0.77	0.25	–104.41
*H_2NOH	–109.14	1.13	0.21	–108.21
*NH_2	–99.98	0.66	0.15	–99.48
*NH_3	–104.03	1.03	0.14	–103.14

Table S6 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on Si site with N-end configuration of NO adsorption, using a 4×4 supercell.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NO	–204.74	0.18	0.17	–204.73
*HNO	–208.89	0.47	0.18	–208.6
*HNOH	–213.00	0.77	0.21	–212.43
*H_2NOH	–217.24	1.13	0.21	–216.32
*NH_2	–208.06	0.65	0.17	–207.58
*NH_3	–212.13	1.03	0.15	–211.25

Table S7 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on Si site with N-end configuration of NO adsorption after including the solvation effects.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NO	–120.98	0.16	0.18	–121.00
*HNO	–125.26	0.47	0.14	–124.93
*HNOH	–129.45	0.78	0.22	–128.90
*H_2NOH	–133.86	1.15	0.19	–132.90
*NH_2	–124.41	0.64	0.08	–123.85
*NH_3	–128.93	1.06	0.11	–127.98

Table S8 Computed NORR free energy changes (Δ*G*) of elementary steps for NORR

on Si site along the N-alternating pathway under different calculation conditions. The unit is eV.

Elementary Reactions	DFT	DFT + U	DFT	DFT + solvation
	3×3	3×3	4×4	3×3
NO (g) + * → *NO	–0.5	–0.66	–0.46	–0.53
*NO + H^+ +e^- → *HNO	–0.4	–0.34	–0.43	–0.48
*HNO + H^+ +e^- → *HNOH	–0.42	–0.39	–0.39	–0.52
*HNOH + H^+ +e^- → *H_2NOH	–0.4	–0.36	–0.44	–0.56
*H_2NOH + H^+ +e^- → *NH_2 + H_2O	–2.04	–2.04	–2.04	–1.72
*NH_2 + H^+ +e^- → *NH_3	–0.23	–0.21	–0.22	–0.68

Table S9 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of NORR intermediates on pure Cu(111) surface.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)

*NO	–196.20	0.16	0.13	–196.17
*NOH	–199.63	0.45	0.16	–199.33
*N	–189.42	0.08	0.03	–189.37
*NH	–194.42	0.29	0.01	–194.14
*NH_2	–198.61	0.69	0.08	–197.99
*NH_3	–202.80	1.01	0.18	–201.97

Table S10 Computed total energies (E), zero-point energies (E_{ZPE}) and entropy (TS) of NORR intermediates on Si@Cu(111) surface.

	E (eV)	E_{ZPE} (eV)	TS (eV)	G (eV)
N-alternating				
*NO	–198.05	0.16	0.19	–198.07

*HNO	–201.97	0.46	0.14	–201.65
*HNOH	–206.14	0.75	0.26	–205.65
*H_2NOH	–210.29	1.11	0.23	–209.41
*NH_2	–201.17	0.65	0.15	–200.64
*NH_3	–205.11	1.01	0.18	–204.27
		O-distal		
*NO	–198.37	0.16	0.13	–198.35
*NOH	–202.31	0.47	0.14	–201.97
*N	–192.60	0.09	0.03	–192.54
*NH	–197.28	0.39	0.04	–196.93
*NH_2	–201.17	0.65	0.15	–200.64
*NH_3	–205.11	1.01	0.18	–204.27

Table S11 Computed total energies (*E*), zero-point energies (E_{ZPE}) and entropy (*TS*) of the intermediates for N_2 synthesis on Cu_2Si monolayer.

	E (eV)	E_{ZPE} (eV)	*TS* (eV)	*G* (eV)
*NONO	–134.84	0.39	0.25	–134.70
*NONOH	–138.98	0.73	0.29	–138.55
*NNO	–128.62	0.29	0.18	–128.51
*NNOH	–132.95	0.59	0.21	–132.57
* + N_2	–124.01	0.15	0.59	–124.44

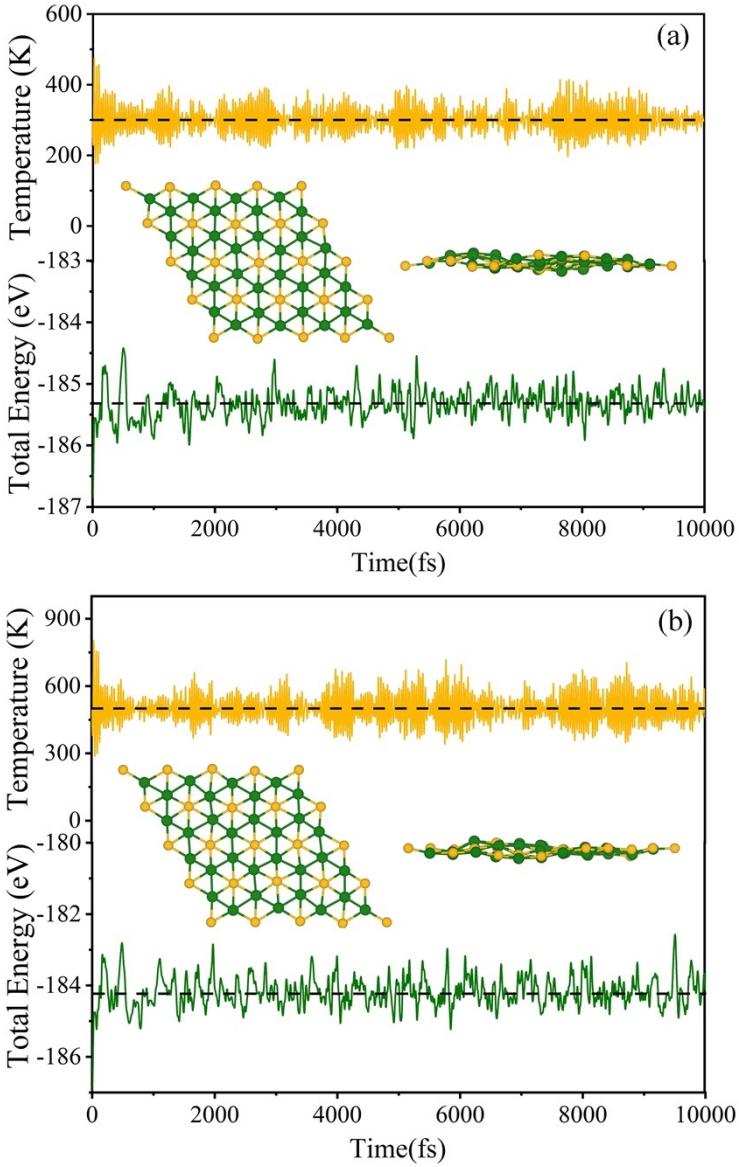

Fig. S1 Variation of total energy and temperature versus the AIMD simulation time for Cu_2Si monolayer at (a) 300 K and (b) 500 K. Insets denote the top and side views of Cu_2Si structure as the AIMD simulations lasted for 10 ps.

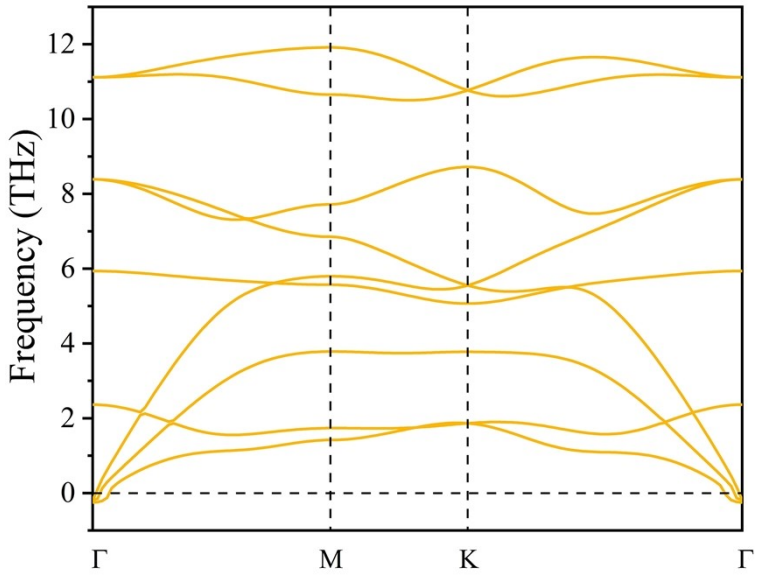

Fig. S2 Phonon dispersion spectrum of Cu_2Si monolayer.

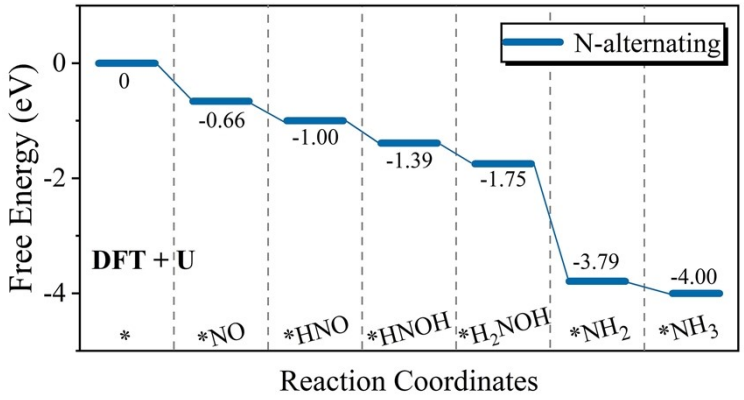

Fig. S3 Free energy diagram for NORR toward NH_3 on Si site by DFT + *U* method.

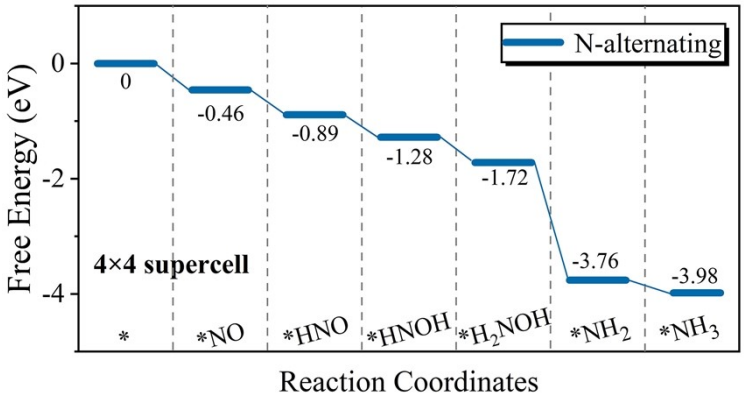

Fig. S4 Free energy diagram for NORR toward NH_3 on Si site using a 4×4 Cu_2Si supercell.

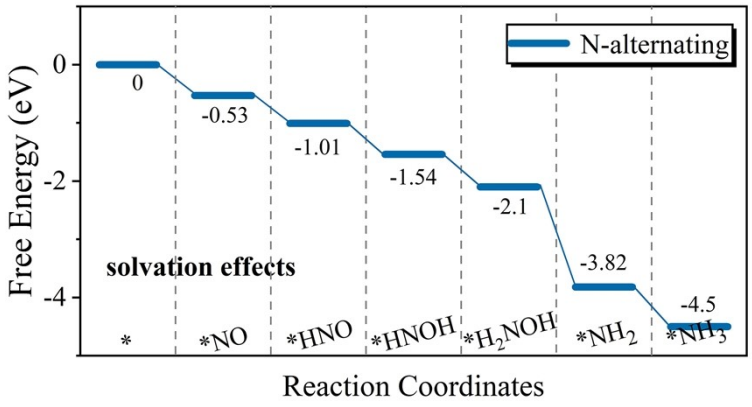

Fig. S5 Free energy diagram for NORR toward NH_3 on Si site using implicit solvation model.