Electronic Supplementary Information

Origin of electrocatalytic nitrogen reduction activity over transition metal disulfides: critical role of *in situ* generation of S vacancy

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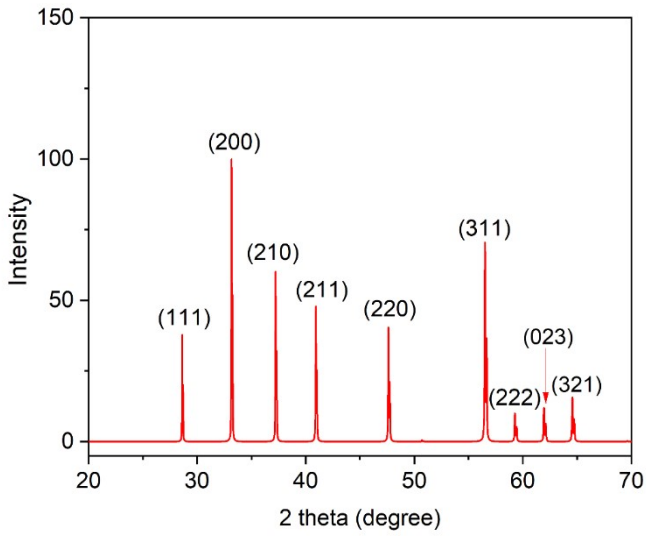

Figure S1 The grazing-incidence X-ray diffraction of FeS_2.[1]

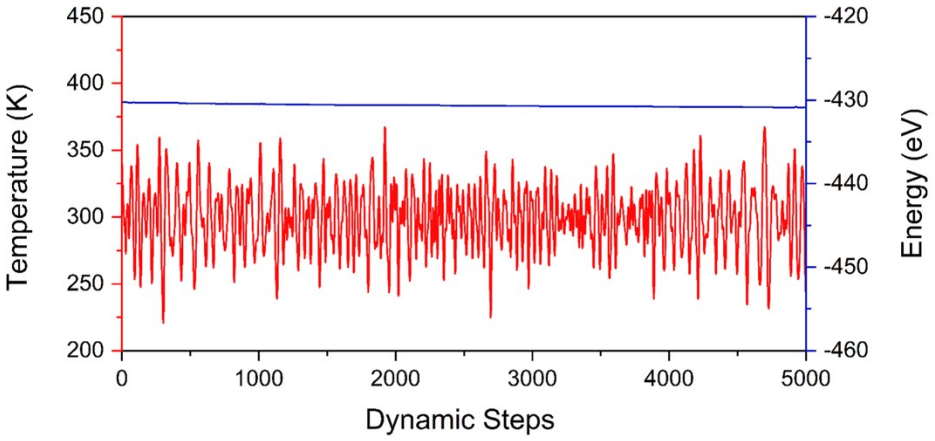

Figure S2 The temperature and energy fluctuations of $FeS_{2-x}(111)$-S_{1V} during 10 ps of *ab initio* molecular dynamics (AIMD) simulations.

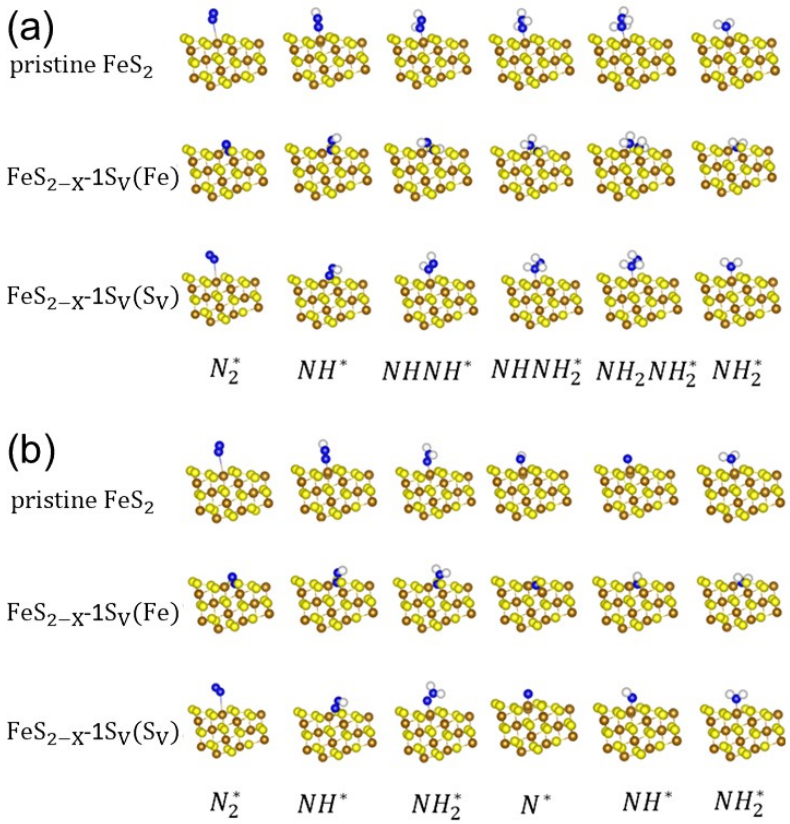

Figure S3 The optimized configurations of the elementary steps on FeS_2(111) and FeS_{2-x}(111)-1S_v *via* (a) the alternating and (b) distal pathways.

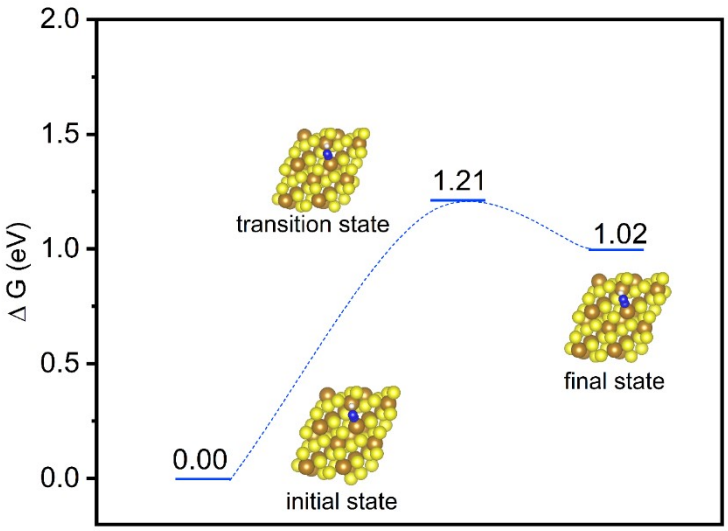

Figure S4 The transition state of N_2*+H*→ NNH* at the Fe site of FeS_{2-x}(111)-1S_V.

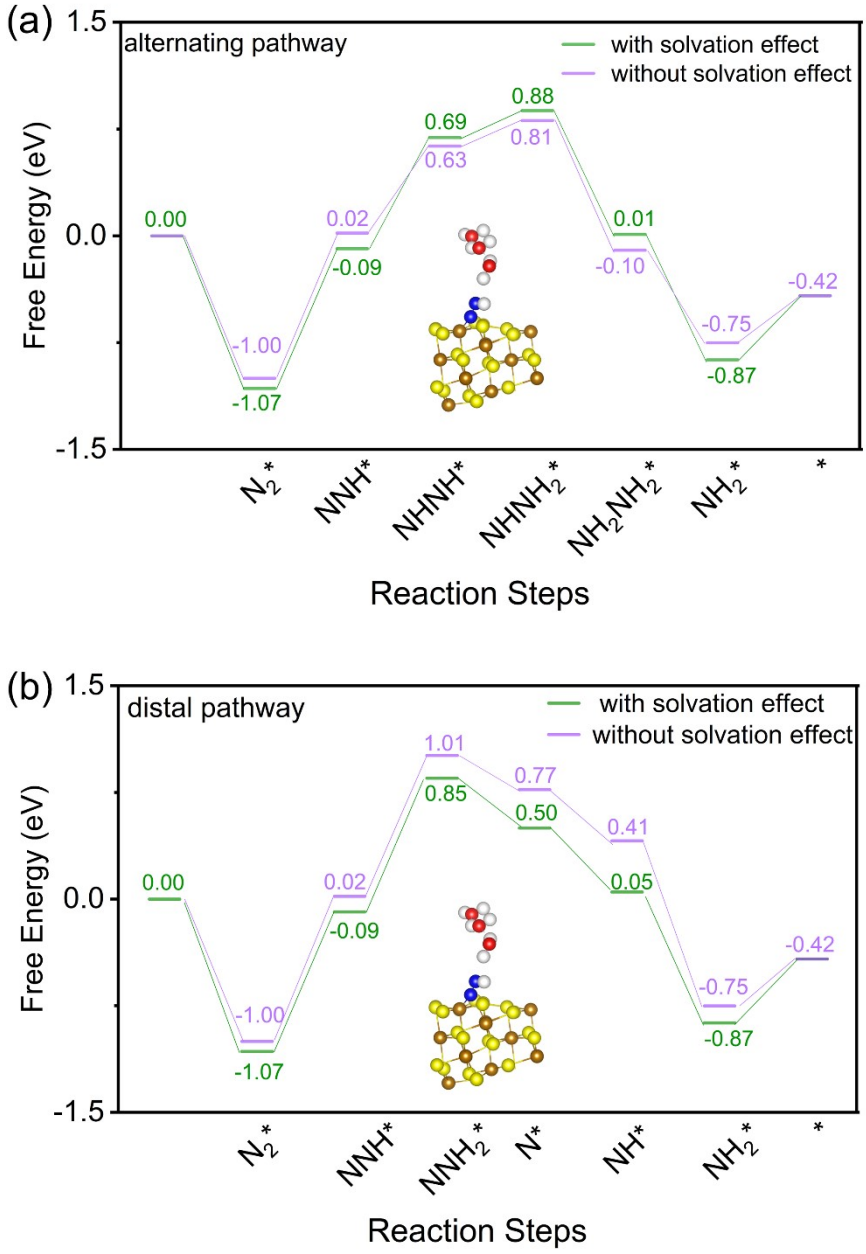

Figure S5 The energy profiles of ENRR over FeS_{2-x}(111)-1S_V surfaces at the Fe active site *via* the (a) associative and (b) distal mechanism with and without solvation effects. The optimized NNH* with explicit water molecules is inserted. The Fe, S, N, O and H are indicated as brown, yellow, blue, red, and white, respectively.

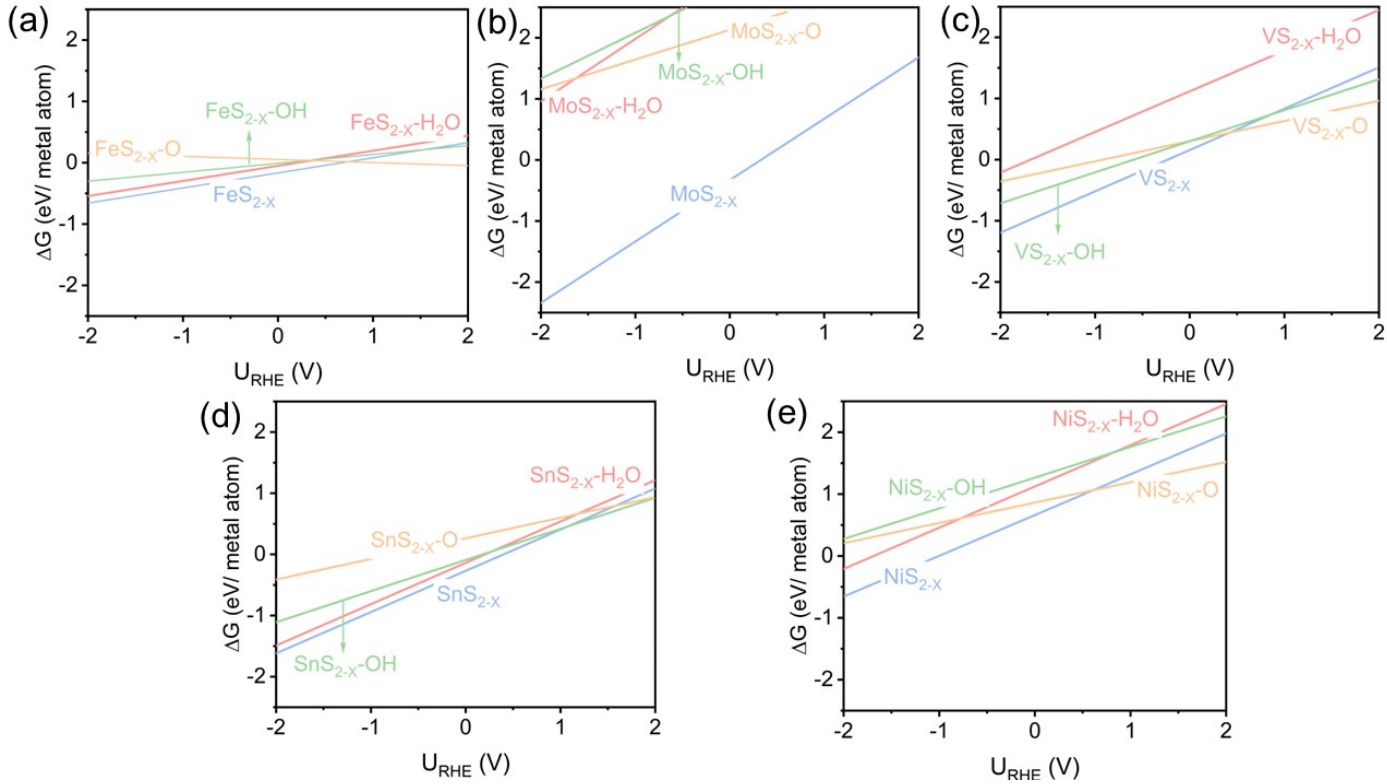

Figure S6 The surface Pourbaix diagrams of occupied H_2O*, HO*, and O* on the TMS_{2-X} surfaces.

Table S1 The highest NH_3 yield, highest Faradic efficiency, and the located potential of FeS_2-based catalysts *via* experimental studies.

Catalysts	NH_3 yield	Faradic efficiency (%)	Potential (V *vs*. RHE)	Refs
FeS_2/MoS_2@rGO	$41.1\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	38.6	-0.2	2
FeS_2	$37.2\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	11.2	-0.5	3
FeS_2/rGO	$27.9\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	6.8	-0.3	4
Sv-FeS_2	$11.5\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	14.6	-0.2	5
MoS_2-FeS_2/Fe foam	$7.1\ \times 10^{-10}\ mol\ s^{-1}\ cm^{-2}$	4.6	-0.5	6
Mo-FeS_2	$25.15\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	14.4	-0.2	7
Sn-FeS_2	15.8 mg h^{-1} cm^{-2}	96.7	-0.5	8

Table S2 The calculated surface energies of different FeS_2 facets.

Facet	E^{unr} (eV)	E^{real} (eV)	a (Å)	b (Å)	Surface energy (J/m^2) unrelaxed	relaxed
111	-180.26	-181.54	10.93	7.00	1.17	1.03
200	-88.48	-89.27	4.44	5.41	2.40	2.14
210	-174.47	-176.80	10.93	7.00	1.77	1.53
211	-173.57	-176.36	10.93	7.00	1.86	1.57
311	-169.66	-172.44	10.93	7.00	2.27	1.98

Table S3 The free energies of NNH* formation, NH_3* formation, and NH_3* desorption on FeS_{2-x}.

Reaction step	Free energy (eV)
$N_2^* + H^* \rightarrow NNH^*$	1.02
$NH_2^* + H^* \rightarrow NH_3^*$	-0.51
$NH_3^* \rightarrow NH_3\ (g)$	0.84

Table S4. The adsorption free energies of N_2 and NH_3 on FeS_{2-x} surface.

Species	N_2	NH_3
Adsorption free energy (eV)	-1.00	-0.51

Table S5 The energy barrier of N_2 adsorption and NNH* formation over FeS_{2-x}(111)-1S_V surfaces at Fe active site with and without U correction.

	ΔG-DFT (eV)	ΔG-DFT+U (eV)
+N_2→NN	-1.00	-1.06
NN*+H*→NNH*	1.02	1.11

Table S6 The highest NH_3 yield, highest Faradic efficiency, and the located potential of TMS_2-based catalysts *via* experimental studies.

Catalysts	NH_3 yield	Faradic efficiency (%)	Potential (V *vs*. RHE)	Refs
B-VS_2	$55.7\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	16.4	-0.4	9
Mo-SnS_2	$41.3\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	20.8	-0.4	10
V-NiS_2	$47.63\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	9.37	-0.35	11
Sv-MoS_2	$29.28\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	8.34	-0.4	12
MoS_2-PDR	$43.4 \pm 3\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	16.8 ± 2	-0.3	13
Sv-MoS_2	$23.38\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	17.9	-0.35	14
Li-S/MoS_2	$43.4\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	9.81	-0.2	15
MoS_2/C_3N_4	$18.5\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	17.5	-0.3	16
Sn-SnS_2	$23.8\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	6.5	-0.7	17
MoS_2-rGO	$24.82\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	4.56	-0.45	18
MoS_2/CN	$36.1\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	15.2	-0.5	19
Fe-MoS_2	$20.11\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	15.72	-0.35	20
FL-VS_2	$34.62\ \mu g\ h^{-1}\ mg_{cat}^{-1}$	2.09	-0.6	21

Table S7 Formation free energies of the occupying species on FeS_{2-x} at -0.2 V_{RHE}.

Species	H_2O*	HO*	O*	N_2*
Formation free energy (eV)	0.55	0.93	2.09	-1.00

Note: The reason for choosing -0.2 V_{RHE} for analysis is because previous works demonstrated that FeS_2 can achieve a high Faradaic efficiency at around -0.2 V_{RHE}.[5] The formation free energy (ΔE_{form}) of occupied species on FeS_{2-x} surface was calculated *via* Eq. (1):

$$\Delta E_{form} = E_{H_mO*} + (2-m)*(0.5*E_{H2} - U_{SHE} - 2.303*k*T*pH) - E_{FeS_{2-x}} - E_{H2O} \quad (1)$$

where m is the number of H of occupied species (H_2O*, HO*, and O*). E_{H2O}, E_{H2}, $E_{FeS_{2-x}}$, and E_{H_mO*} are the energies of H_2O molecule, H_2 molecule, FeS_{2-x} surface, and FeS_{2-x} surfaces with adsorbed species, respectively. U_{SHE}, k_B, and T are the potential under the scale of standard hydrogen electrode (SHE), the Boltzmann constant, and temperature, respectively.

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