Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

N, S coordination in Ni single atom catalyst promoting CO_2RR towards HCOOH

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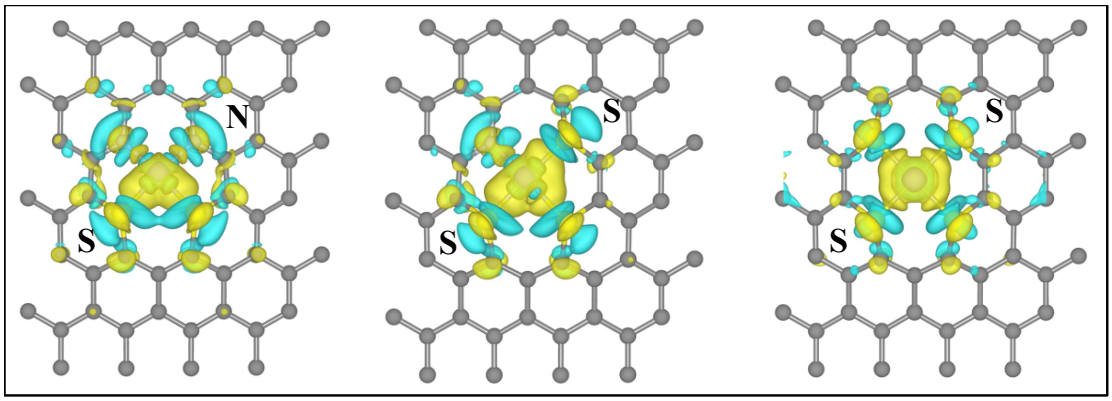
Figure S1. Optimized structures of (a) NiN_2S_2-1, (b) NiN_1S_3, and (c) NiS_4.

Figure S2. Charge density difference of NiN_2S_2-1, NiN_1S_3, and NiS_4. Yellow and cyan regions represent increasing and decreasing electron densities, respectively, and the isosurface values were 2×10^{-3} e per $Bohr^3$.



NiN_2S_2-1 **NiN_1S_3** **NiS_4**

Figure S3. Optimized adsorption configurations and adsorption energies of CO_2 on NiN_4 under different potentials.

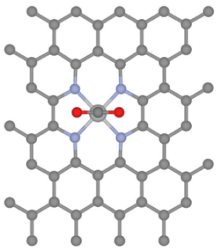
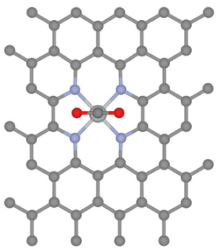
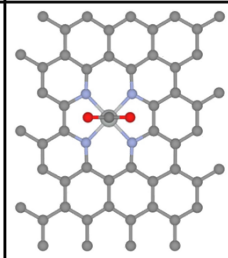
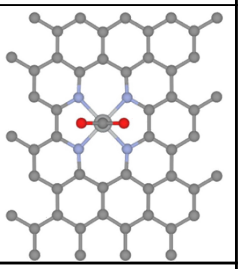
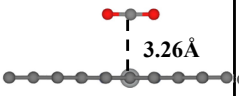
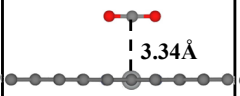
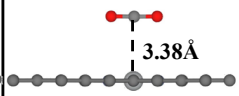
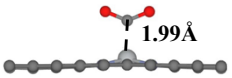
potentials	0V	-0.23V	-0.54V	-0.84V
top-view				
Side-view	 3.26Å $CO_{2\ ads}$ -0.58eV	 3.34Å $CO_{2\ ads}$ -0.71eV	 3.38Å $CO_{2\ ads}$ -0.64eV	 1.99Å $CO_{2\ ads}$ -0.37eV

Figure S4. Free energy profiles of CO_2RR to (a) CO and (b) HCOOH on NiN_2S_2-1, NiN_1S_3, and NiS_4.

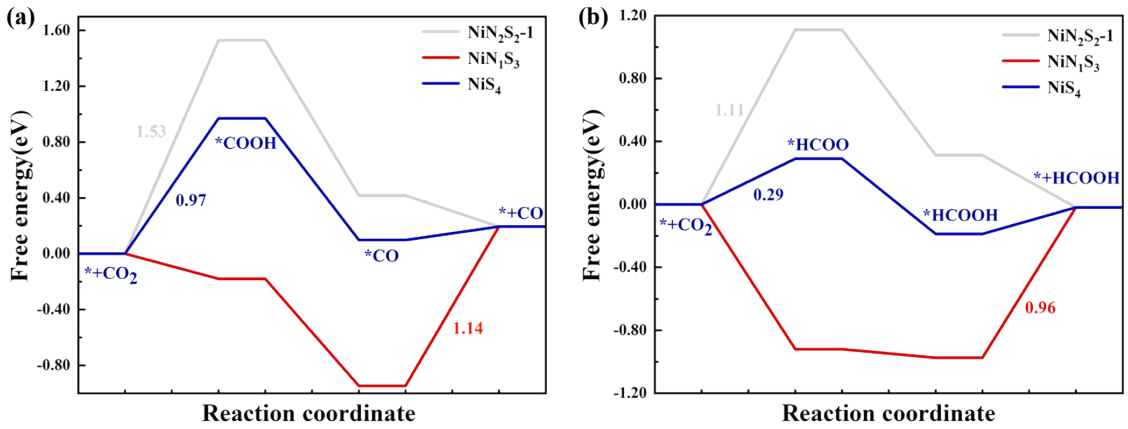


Figure S5. Optimized adsorption configurations of CO_2 and H on NiN_4, NiN_3S_1, and NiN_2S_2.

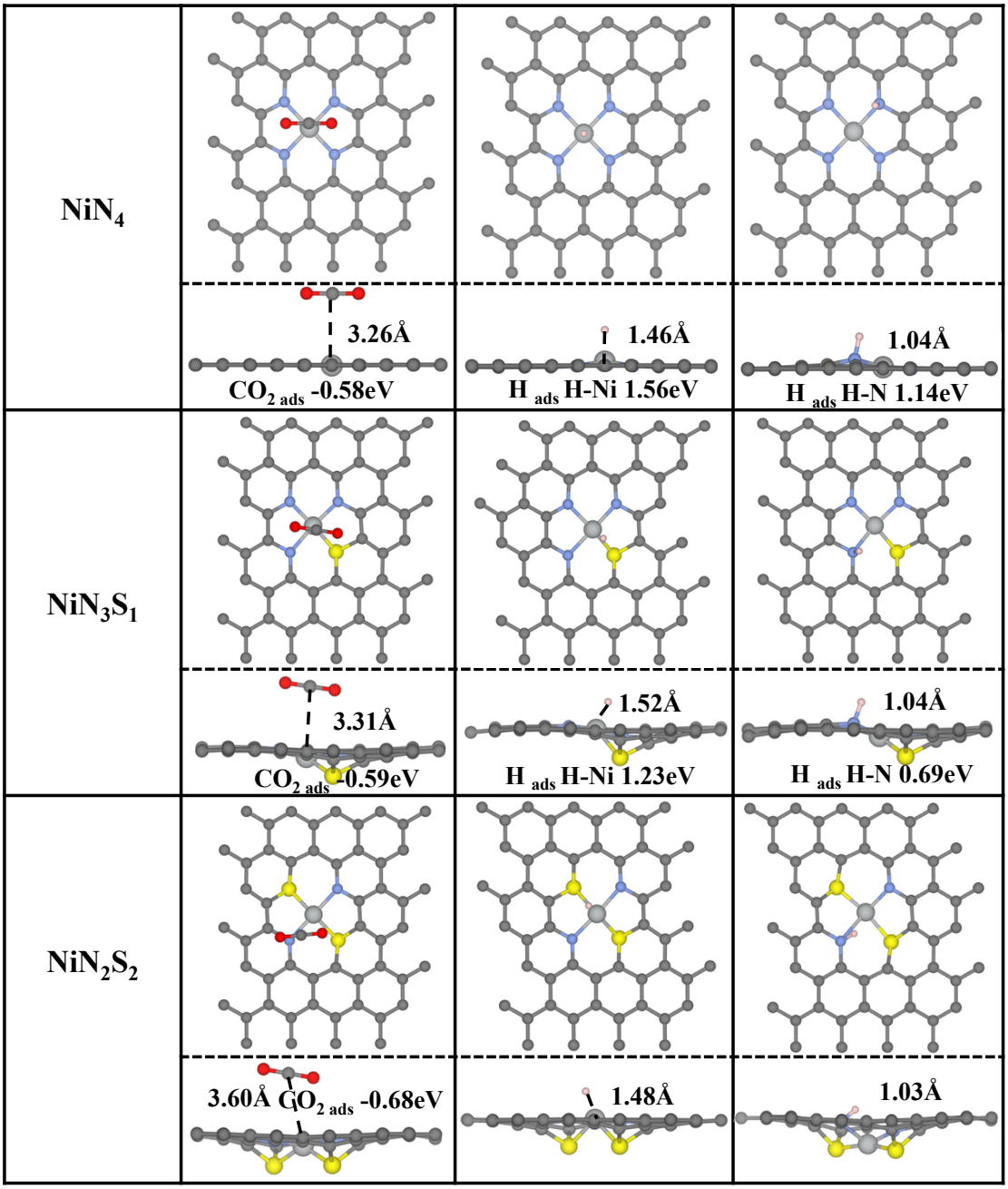


Figure S6. (a) Summary of limiting potential ($U_L^{CO_2RR}$) of products for the CO and HCOOH productions on NiN_2S_2-1, NiN_1S_3 and NiS_4. (b) Limiting potential difference between CO_2RR and HER ($U_L^{CO_2RR} - U_L^{HER}$).

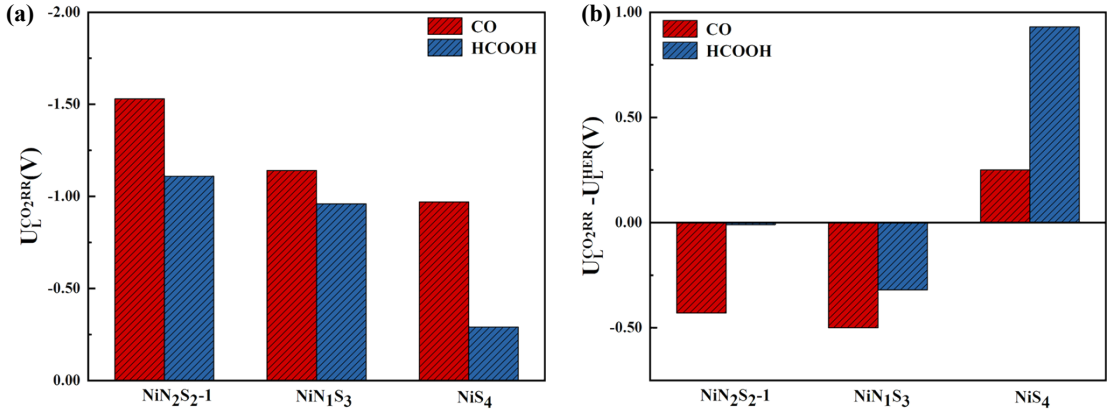


Table S1. Cohesive energy E_{coh}, formation energies E_f, and dissolution potential U_{diss} of NiN_xS_y.

NiN_xS_y	E_{coh} (eV)	E_f (eV)	U_{diss}(V)
NiN_4	9.03	-6.39	2.93
NiN_3S_1	8.89	-4.57	2.02
NiN_2S_2	8.76	-2.62	1.05
NiN_2S_2-1	8.78	-4.37	1.93
NiN_1S_3	8.64	-2.28	0.88
NiS_4	8.52	-2.69	1.09

Table S2. Proposed elementary steps and free energy changes for CO_2RR pathways on NiN_4, NiN_3S_1, and NiN_2S_2 at 0 V versus SHE.

Elementary step	ΔG/eV		
	NiN_4	NiN_3S_1	NiN_2S_2
$CO_2 + H^+ + e^- \rightarrow$*COOH	1.47	1.19	0.57
*COOH + $H^+ + e^- \rightarrow$ *CO + H_2O	-0.95	-0.90	-0.91
*CO → CO + *	-0.64	-0.10	0.53
*$CO_2 + H^+ + e^- \rightarrow$ *HCOO	1.14	0.50	-0.18
*HCOO + $H^+ + e^- \rightarrow$ *HCOOH	-0.66	-0.10	0.24
*HCOOH → HCOOH + *	-0.43	-0.42	-0.08

Table S3. Summary of CO_2RR potential determining steps (PDS), limiting potential ($U_L^{CO_2RR}$) of CO_2RR and limiting potential difference between CO_2RR and HER ($U_L^{CO_2RR} - U_L^{HER}$) on NiN_4, NiN_3S_1 and NiN_2S_2.

Catalysts	Products	PDS	ΔG/eV	$U_L^{CO_2RR}$ / V vs RHE	$U_L^{CO_2RR} - U_L^{HER}$ / V vs RHE
NiN_4	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.47	-1.47	-0.33
	HCOOH	$*CO_2 + H^+ + e^- \rightarrow *HCOO$	1.14	-1.14	0
NiN_3S_1	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.19	-1.19	-0.50
	HCOOH	$*CO_2 + H^+ + e^- \rightarrow *HCOO$	0.50	-0.50	0.19
NiN_2S_2	CO	$CO_2 + H^+ + e^- \rightarrow *COOH$	0.57	-0.57	-0.20
	HCOOH	$*HCOO + H^+ + e^- \rightarrow *HCOOH$	0.24	-0.24	0.13

Table S4. Summary of CO_2RR potential determining steps (PDS), limiting potential ($U_L^{CO_2RR}$) of CO_2RR and limiting potential difference between CO_2RR and HER ($U_L^{CO_2RR} - U_L^{HER}$) on NiN_2S_2-1, NiN_1S_3 and NiS_4.

Catalysts	Products	PDS	ΔG/eV	$U_L^{CO_2RR}$ / V vs RHE	$U_L^{CO_2RR} - U_L^{HER}$ / V vs RHE
NiN_2S_2-1	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.53	-1.53	-0.43
	HCOOH	$*CO_2 + H^+ + e^- \rightarrow *HCOO$	1.11	-1.11	-0.01
NiN_1S_3	CO	$*CO \rightarrow * + CO$	1.14	-1.14	-0.50
	HCOOH	$*HCOOH \rightarrow * + HCOOH$	0.96	-0.96	-0.32
NiS_4	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	0.97	-0.97	0.25
	HCOOH	$*CO_2 + H^+ + e^- \rightarrow *HCOO$	0.29	-0.29	0.93