Electronic Supplementary Information

Surface selectivity of Ni_3S_2 toward hydrogen evolution reaction: a first-principles study

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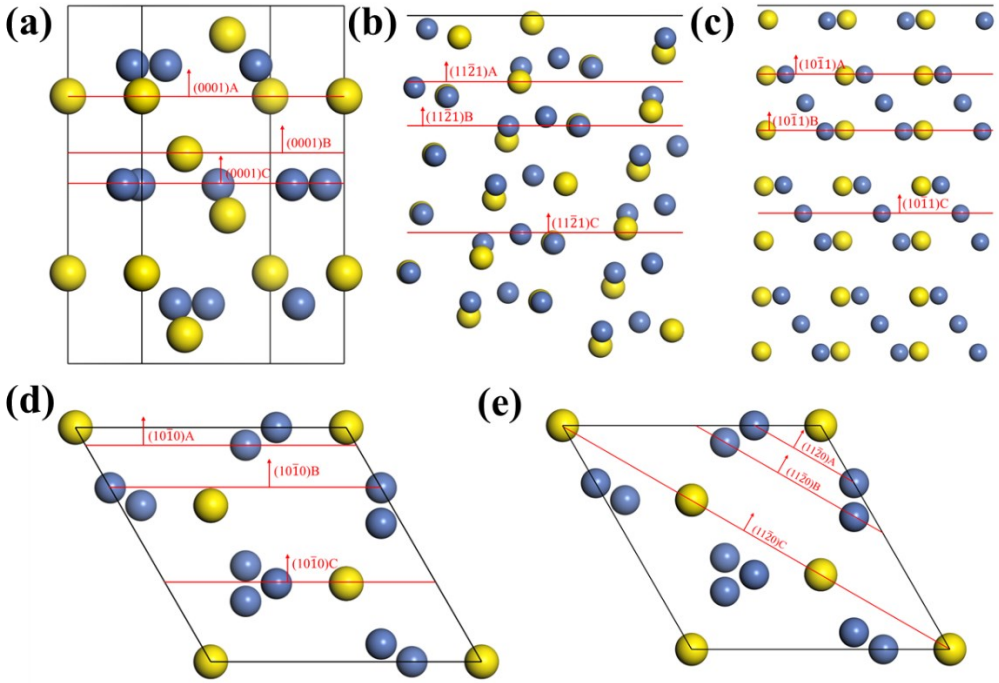

Fig. S1 The (a) (0001), (b) $(10\bar{1}0)$, (c) $(10\bar{1}1)$, (d) $(11\bar{2}0)$ and (e) $(11\bar{2}1)$ planes with different terminations. These surfaces were selected for the calculation based on the consideration of symmetry of lattice. The surfaces with different terminations are denoted as A, B and C.

As shown in **Fig. S1**, in order to study the HER properties of different surfaces with different terminations, six relatively thermodynamically stable surfaces were selected based on the consideration of symmetry of low-index planes. To simplify the calculation process, all the considered surfaces are denoted as (0001)A, (0001)B, (0001)C of (0001) planes, $(10\bar{1}0)$A, $(10\bar{1}0)$B, $(10\bar{1}0)$C of $(10\bar{1}0)$ planes, $(10\bar{1}1)$A, $(10\bar{1}1)$B, $(10\bar{1}1)$C of $(10\bar{1}1)$ planes, $(11\bar{2}0)$A, ($11\bar{2}0)$B, $(11\bar{2}0)$C of $(11\bar{2}0)$ planes, and $(11\bar{2}1)$A, $(11\bar{2}1)$B, $(11\bar{2}1)$C of $(11\bar{2}1)$ planes.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S2.**

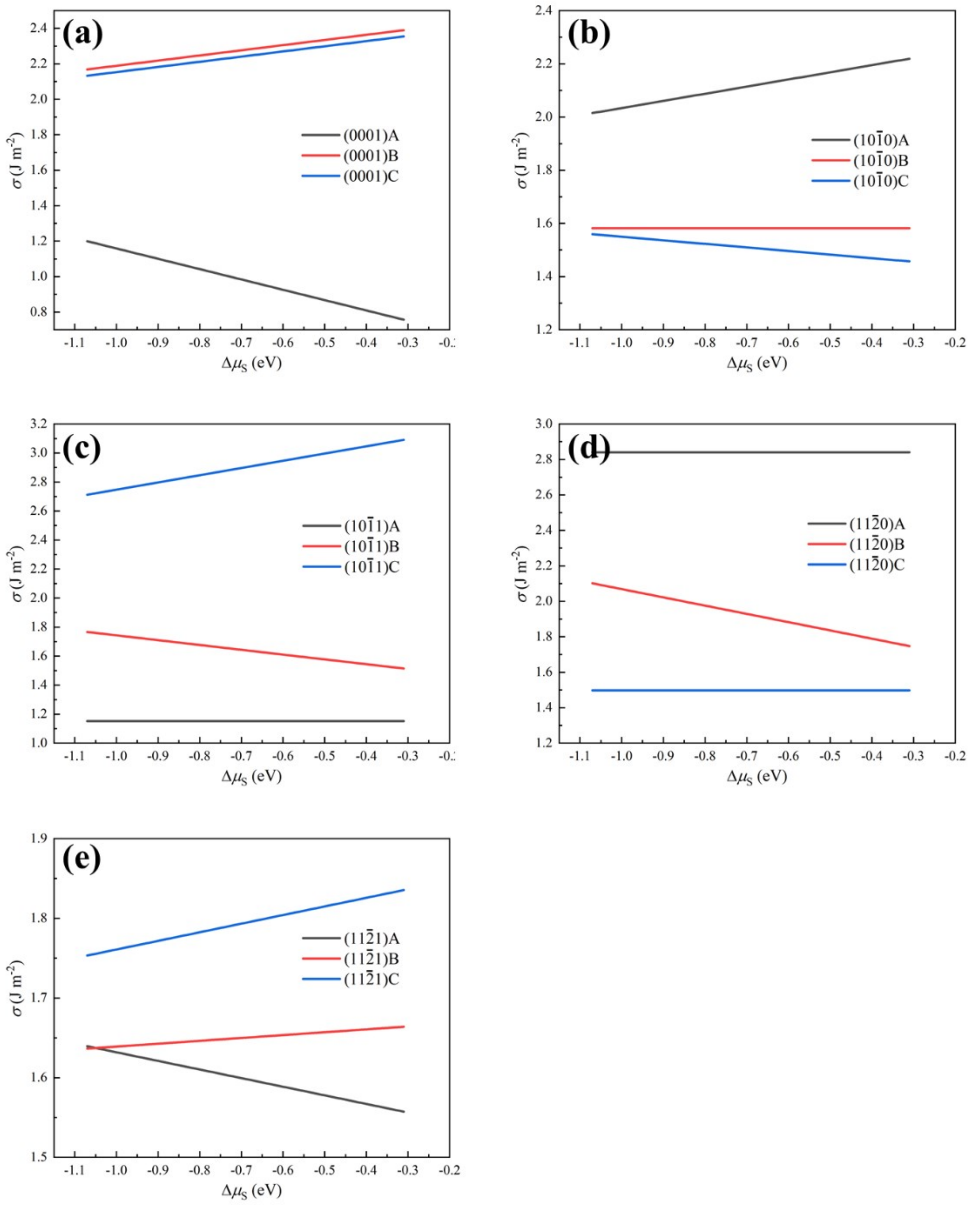

Fig. S2 The surface energies of all the considered surfaces. (a) (0001)A, (0001)B and (0001)C of (0001) planes. (b) $(10\bar{1}0)$A, $(10\bar{1}0)$B and $(10\bar{1}0)$C of $(10\bar{1}0)$ planes. (c) $(10\bar{1}1)$A, $(10\bar{1}1)$B and $(10\bar{1}1)$C of $(10\bar{1}1)$ planes. (d) $(11\bar{2}0)$A, $(11\bar{2}0)$B and $(11\bar{2}0)$C of $(11\bar{2}0)$ planes. (e) $(11\bar{2}1)$A, $(11\bar{2}1)$B and $(11\bar{2}1)$C of $(11\bar{2}1)$ planes. A, B and C indicate the surface terminated with different atoms.

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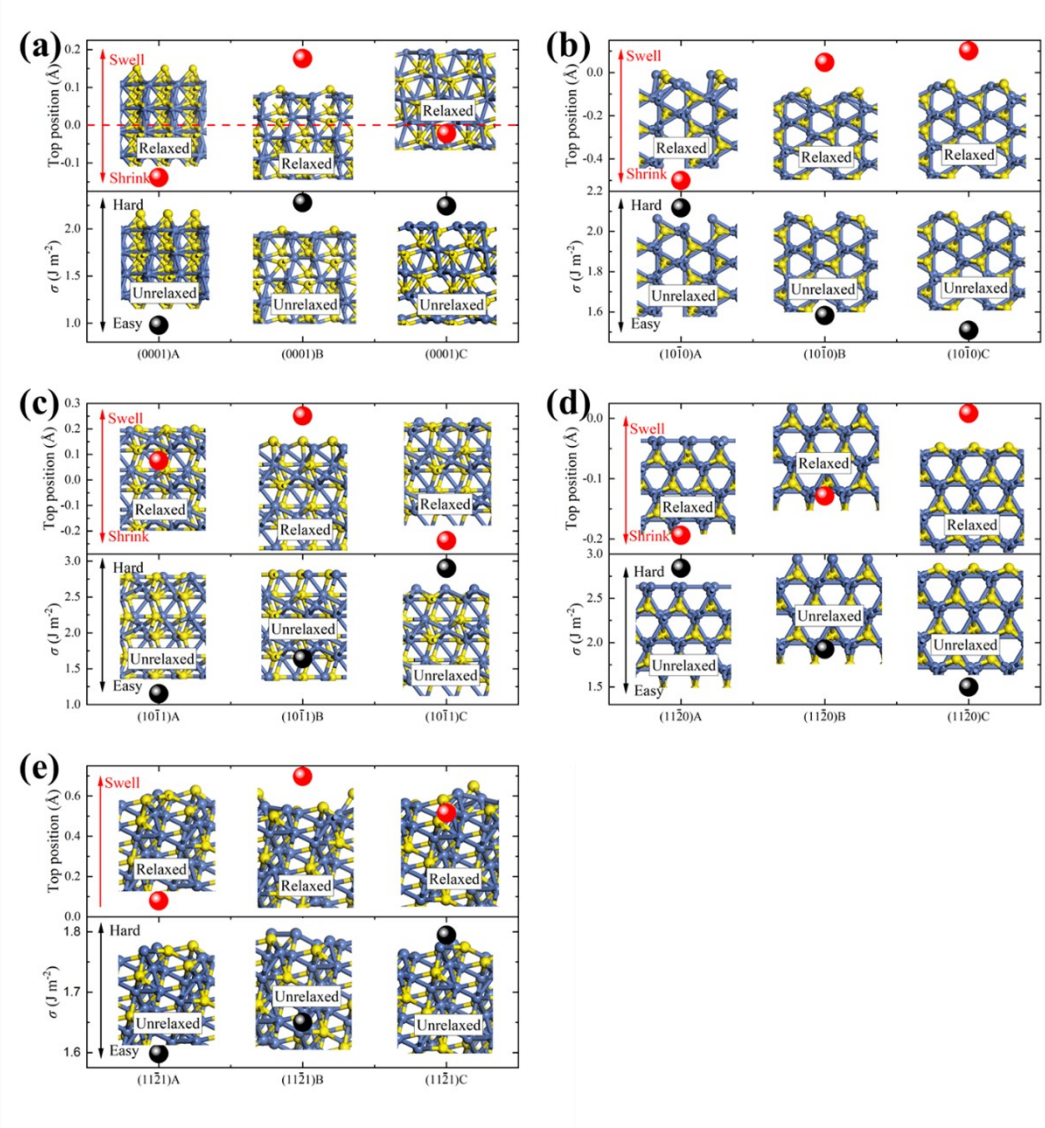

Fig. S3 The changes of the top position of the fifteen stable surfaces and the corresponding surface energies at $\Delta\mu_S = -0.69\ eV$. The side views of relaxed and unrelaxed slabs models are also shown. Yellow and blue spheres in ball-and-stick models stand for S and Ni atoms.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S4.**

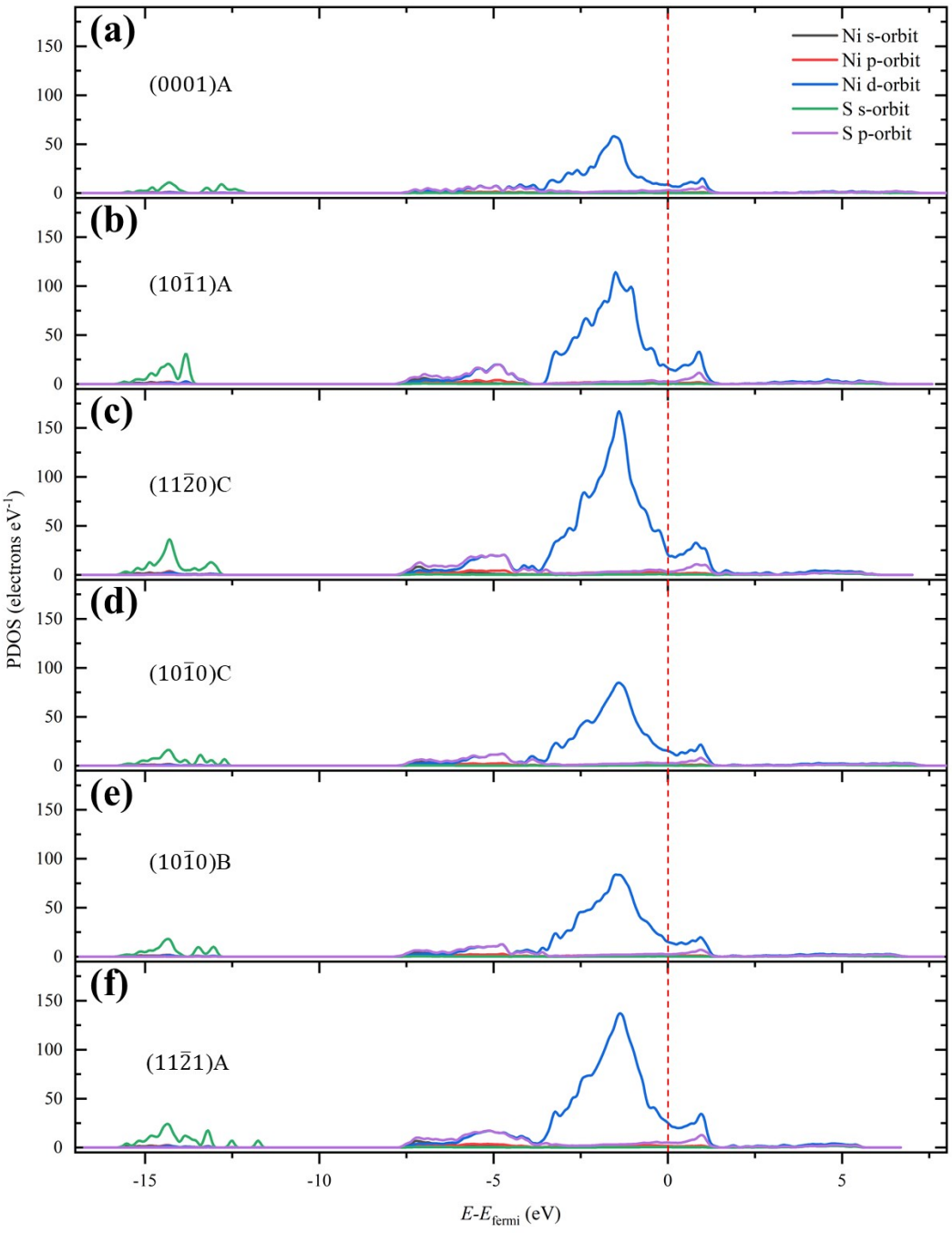

Fig. S4 The PDOS of (a) (0001)A, (b) $(10\bar{1}1)$A, (c) $(11\bar{2}0)$C, (d) $(10\bar{1}0)$C, (e) $(10\bar{1}0)$B and (f) $(11\bar{2}1)$A surfaces of Ni_3S_2.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S5.**

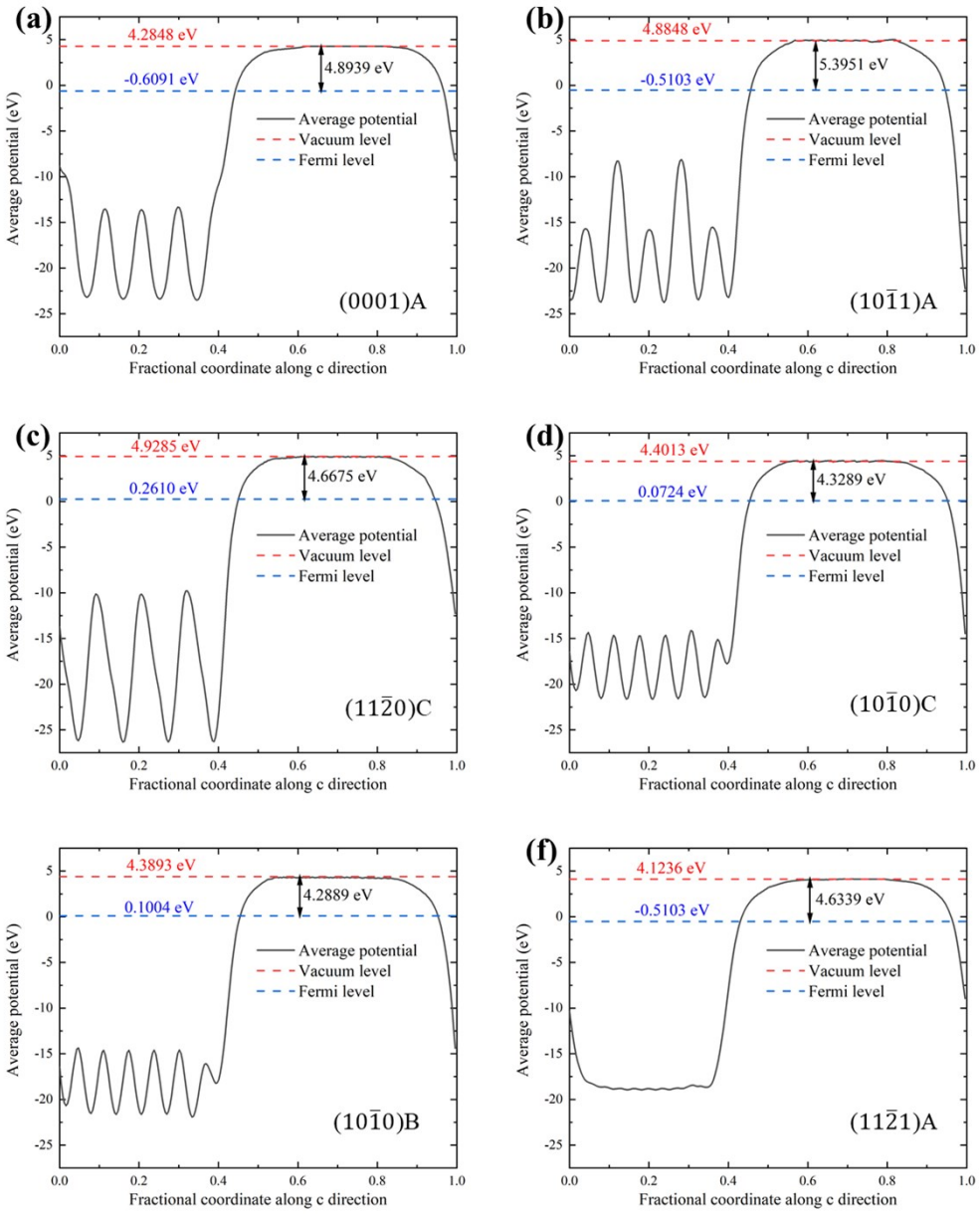

Fig. S5 The work functions of different surfaces of Ni_3S_2. (a) (0001)A, (b) $(10\bar{1}1)$A, (c) $(11\bar{2}0)$C, (d) $(10\bar{1}0)$C, (e) $(10\bar{1}0)$B and (f) $(11\bar{2}1)$A surfaces.

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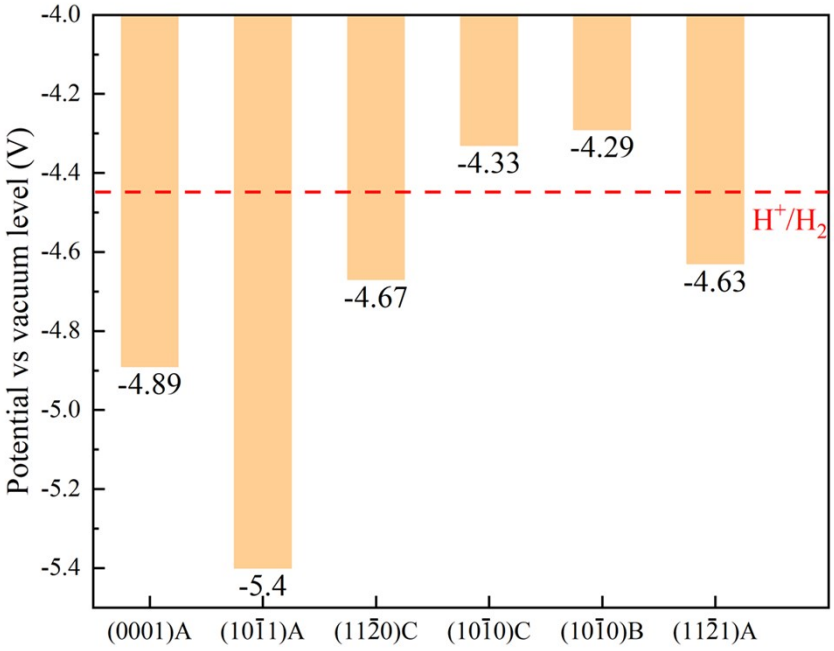

Fig. S6 The potential difference between surfaces of Ni_3S_2 and HER, including (0001)A, $(10\bar{1}1)$A, $(11\bar{2}0)$C, $(10\bar{1}0)$C, $(10\bar{1}0)$B and $(11\bar{2}1)$A surfaces.[1]

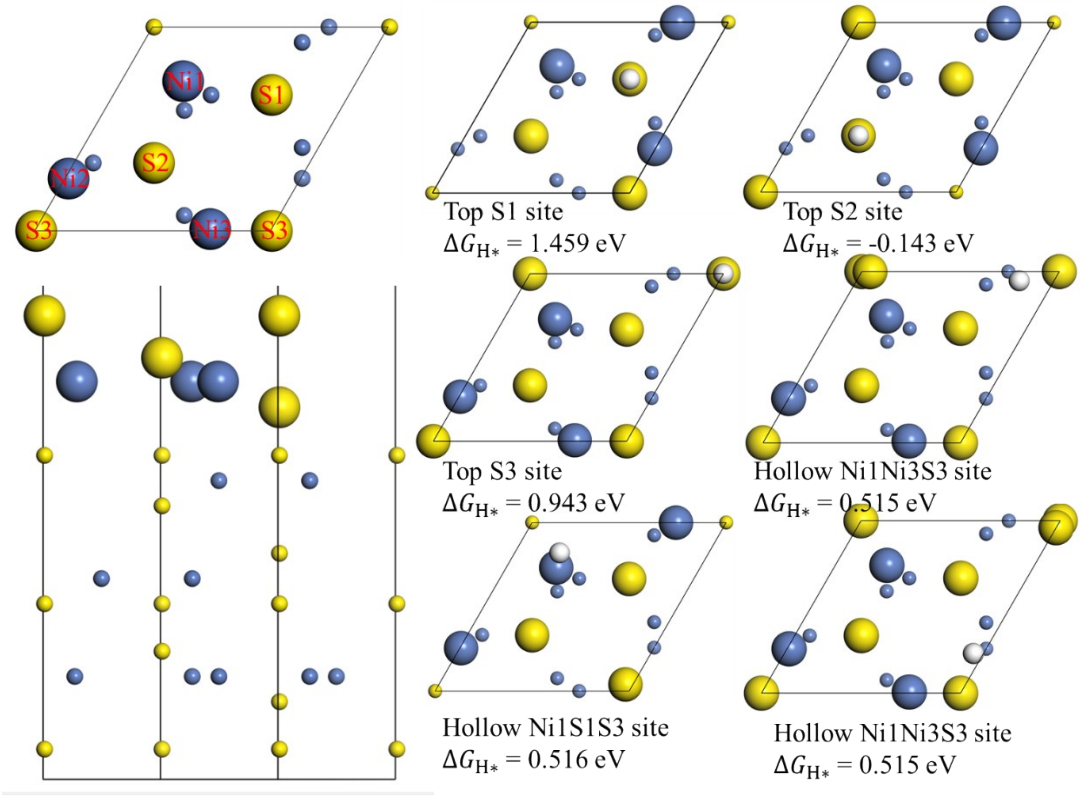

Fig. S7 The details of sites information of $(^{0001})$A of Ni_3S_2.

Table S1 The details of Volmer-Heyrovsky process of (0001)A of Ni_3S_2.

Site before relaxation	**Site after relaxation**	ΔG_{H*} **(eV)**
Top S1	Top S1	1.45933
Top S2	Top S2	-0.14256
Top S3	Top S3	0.94331
Top Ni3	Hollow Ni1Ni3S3	0.51595
Top Ni1	Hollow Ni1S1S3	0.51613
Top Ni2	Hollow Ni2Ni3S3	0.51599

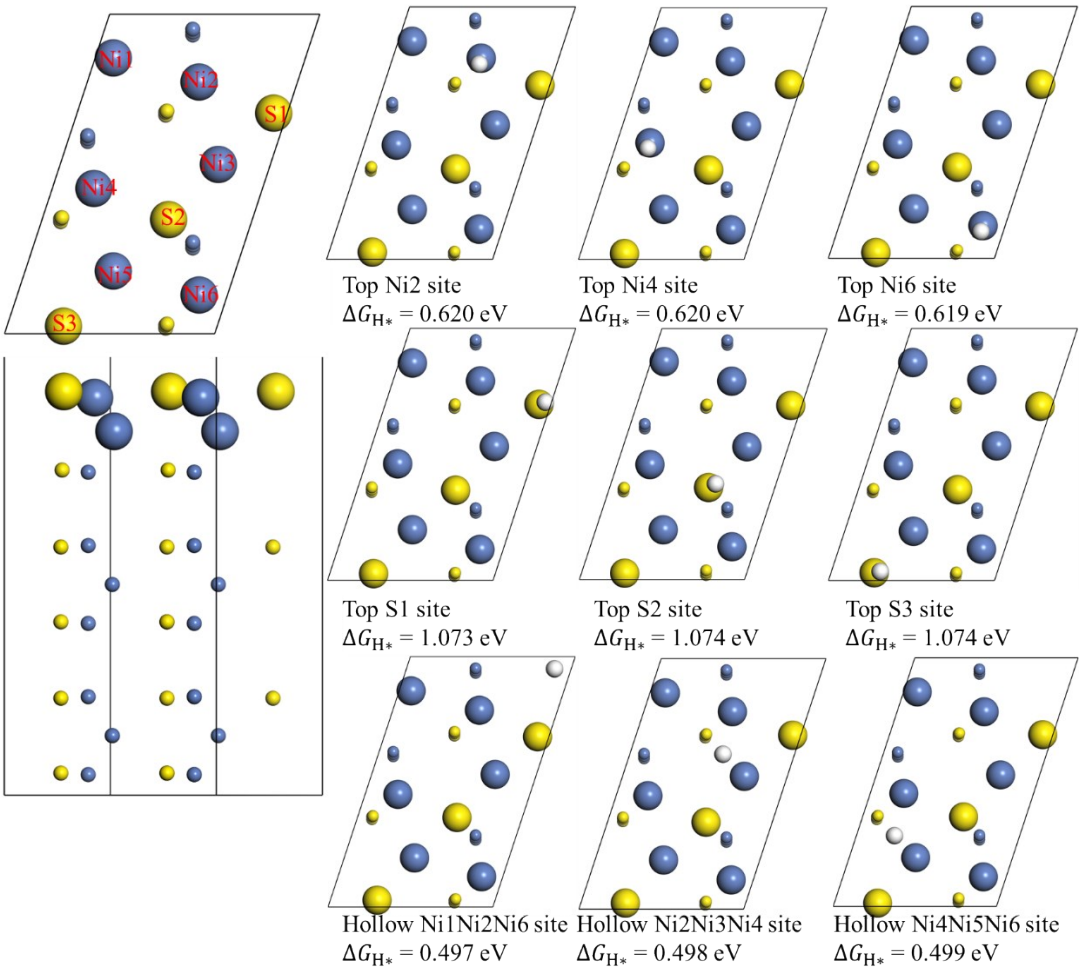

Fig. S8 The details of sites information of $(10\bar{1}1)$A of Ni_3S_2.

Table S2 The details of Volmer-Heyrovsky process of $(10\bar{1}1)$A of Ni_3S_2.

Site before relaxation	Site after relaxation	ΔG_{H*} (eV)
Top Ni2	Top Ni2	0.61978
Top Ni4	Top Ni4	0.61974
Top Ni6	Top Ni6	0.61923
Top S1	Top S1	1.07367
Top S2	Top S2	1.07413
Top S3	Top S3	1.07413
Top Ni1	Hollow Ni1Ni2Ni6	0.49780
Top Ni3	Hollow Ni2Ni3Ni4	0.49807
Top Ni5	Hollow Ni4Ni5Ni6	0.49854

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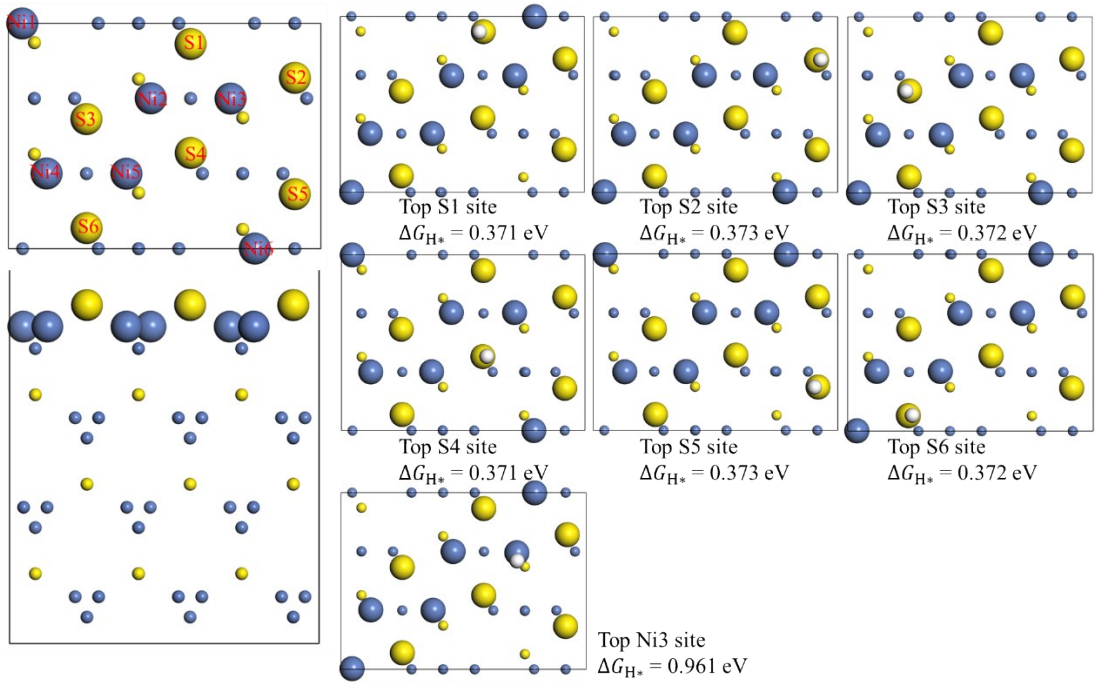

Fig. S9 The details of sites information of $(1\bar{1}20)$C of Ni_3S_2.

Table S3 The details of Volmer-Heyrovsky process of $(11\bar{2}0)$C of Ni_3S_2.

Site before relaxation	**Site after relaxation**	ΔG_{H*} **(eV)**
Top Ni3	Top Ni3	0.96081
Top S1	Top S1	0.37126
Top S2	Top S2	0.37269
Top S3	Top S3	0.37194
Top S4	Top S4	0.37148
Top S5	Top S5	0.37269
Top S6	Top S6	0.37178

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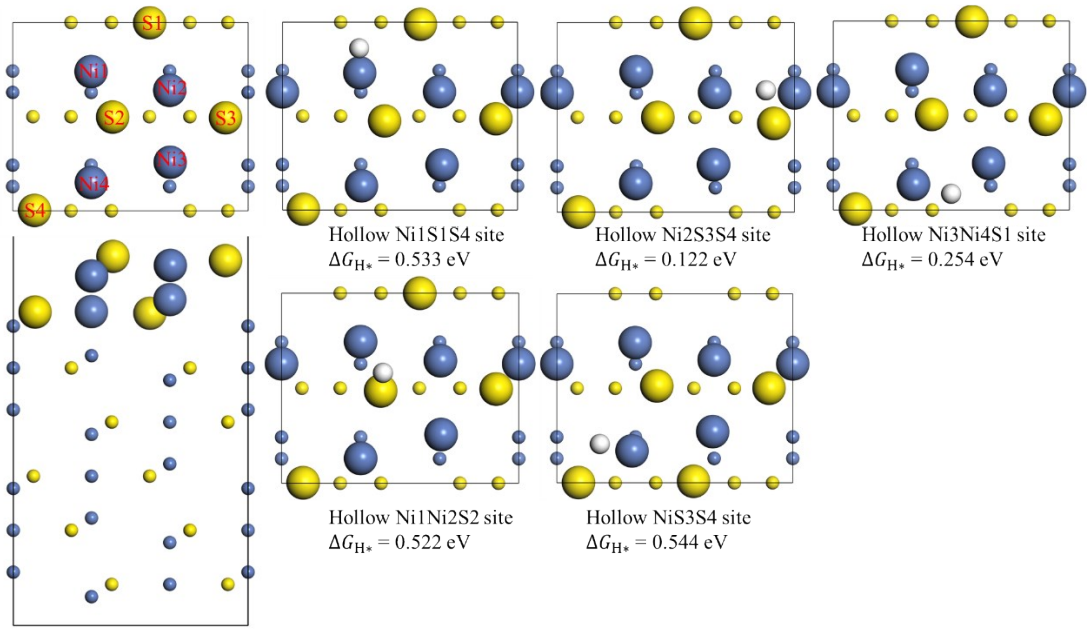

Fig. S10 The details of sites information of $(10\bar{1}0)$C of Ni_3S_2.

Table S4 The details of Volmer-Heyrovsky process of $(10\bar{1}0)$C of Ni_3S_2.

Site before relaxation	Site after relaxation	ΔG_{H*} (eV)
Top S2	Hollow Ni1Ni2S2	0.52232
Top Ni1	Hollow Ni1S1S4	0.53318
Top Ni2	Hollow Ni2S3S4	0.12247
Top Ni3	Hollow Ni3Ni4S1	0.25360
Top S4	Hollow Ni4S3S4	0.54435

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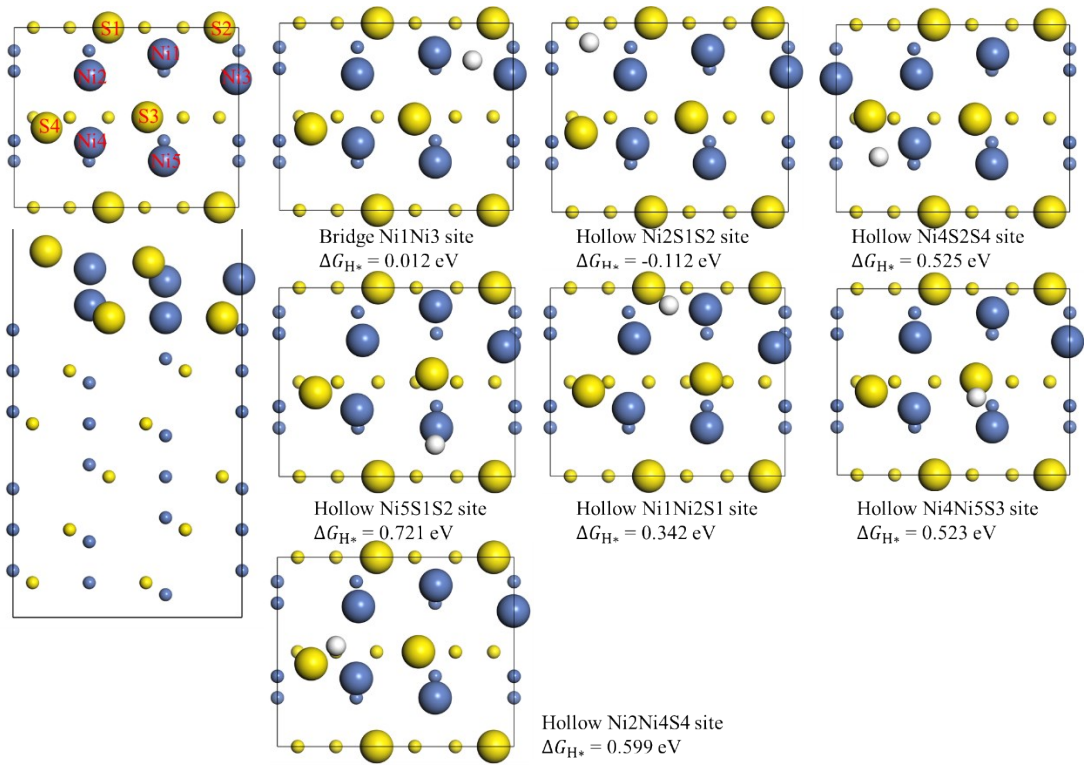

Fig. S11 The details of sites information of $(10\bar{1}0)$B of Ni_3S_2.

Table S5 The details of Volmer-Heyrovsky process of $(10\bar{1}0)$B of Ni_3S_2.

Site before relaxation	Site after relaxation	ΔG_{H*} (eV)
Top Ni1	Bridge Ni1Ni3	0.01249
Top S1	Hollow Ni1Ni2S1	0.34238
Top S4	Hollow Ni2Ni4S4	0.59894
Top Ni2	Hollow Ni2S1S2	-0.11155
Top S3	Hollow Ni4Ni5S3	0.52396
Top Ni4	Hollow Ni4S2S4	0.52533
Top Ni5	Hollow Ni5S1S2	0.72123

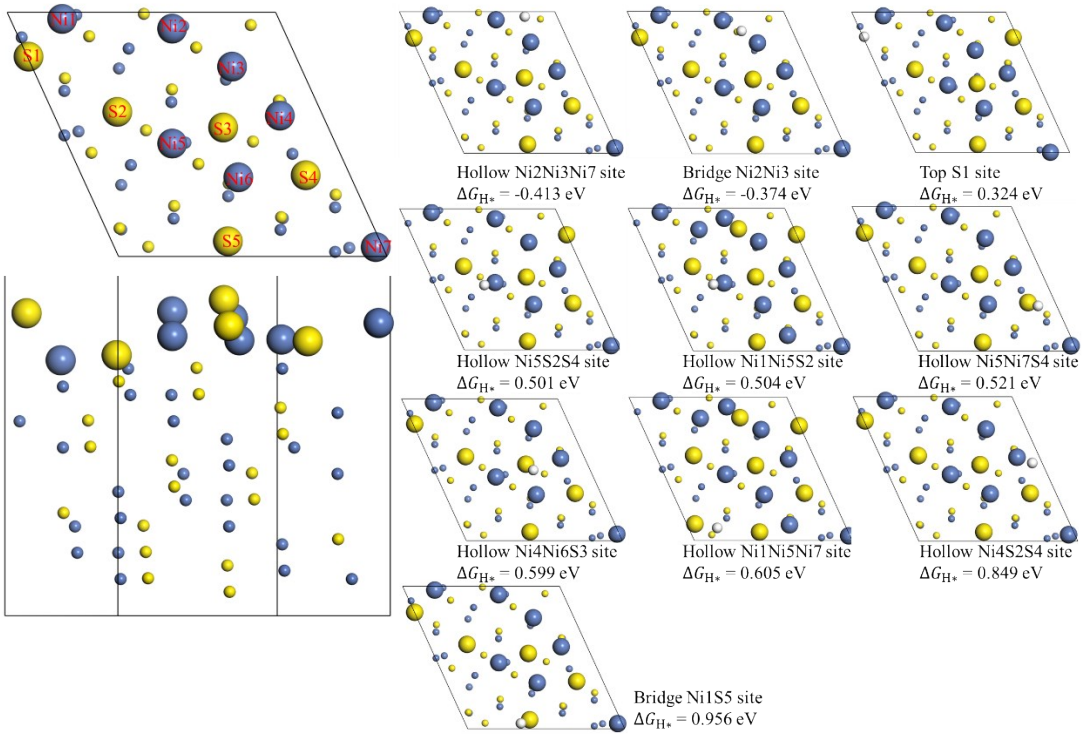

Fig. S12 The details of sites information of $(1\bar{1}21)$A of Ni_3S_2.

Table S6 The details of Volmer-Heyrovsky process of $(11\bar{2}1)$A of Ni_3S_2.

Site before relaxation	Site after relaxation	ΔG_{H*} (eV)
Top S1	Top S1	0.32416
Top S5	Bridge Ni1S5	0.95564
Top Ni2	Bridge Ni2Ni3	-0.37374
Top Ni1	Hollow Ni1Ni5Ni7	0.60532
Top Ni5	Hollow Ni1Ni5S2	0.50377
Top Ni7	Hollow Ni2Ni3Ni7	-0.41345
Top Ni6	Hollow Ni4Ni6S3	0.59948
Top Ni4	Hollow Ni4S2S4	0.84930
Top S4	Hollow Ni5Ni7S4	0.52108
Top S2	Hollow Ni5S2S4	0.50073

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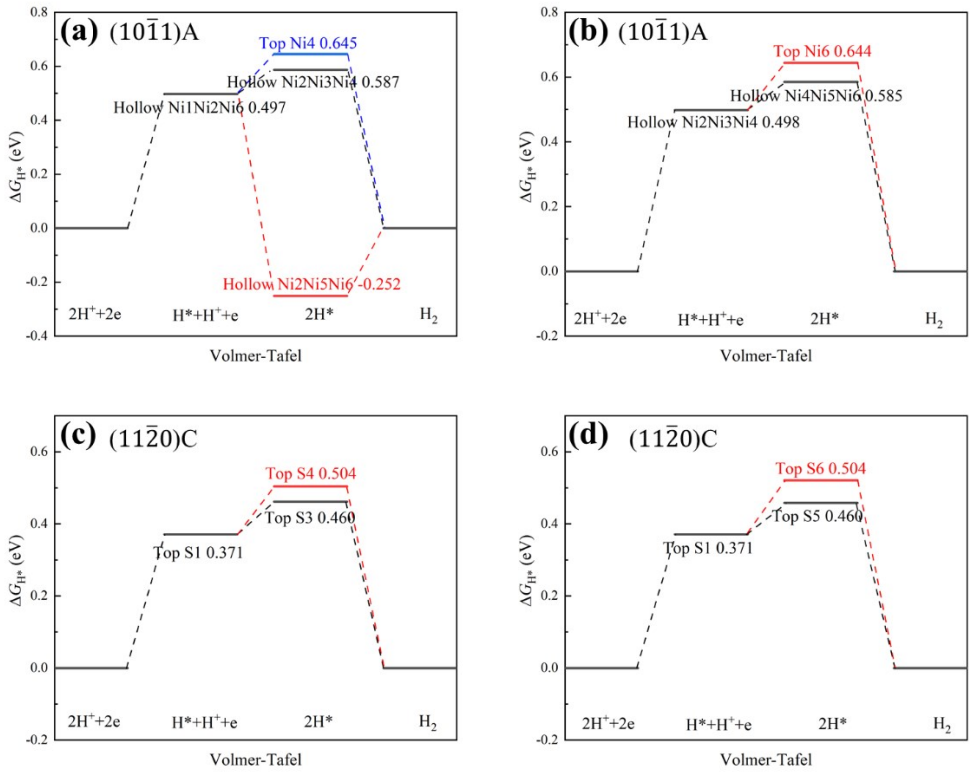

Fig. S13 The adsorption of two hydrogen atoms on (a, b) $(10\bar{1}1)$A and (c, d) $(10\bar{2}0)$C surfaces of Ni_3S_2.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S14.**

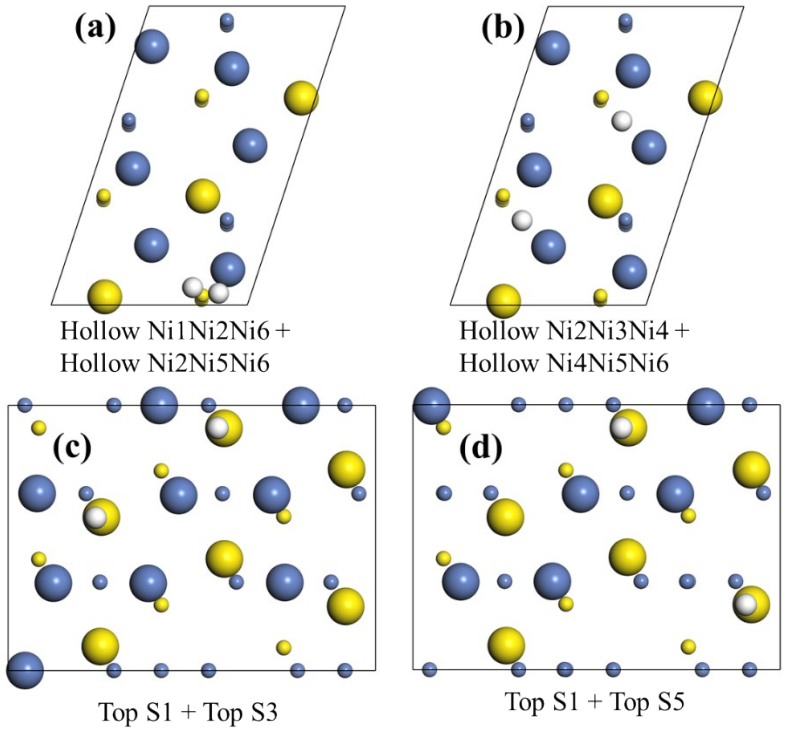

Fig. S14 The most stable sites for the adsorption of two hydrogen atoms for $(10\bar{1}1)$A and $(11\bar{2}0)$C of Ni_3S_2.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S15.**

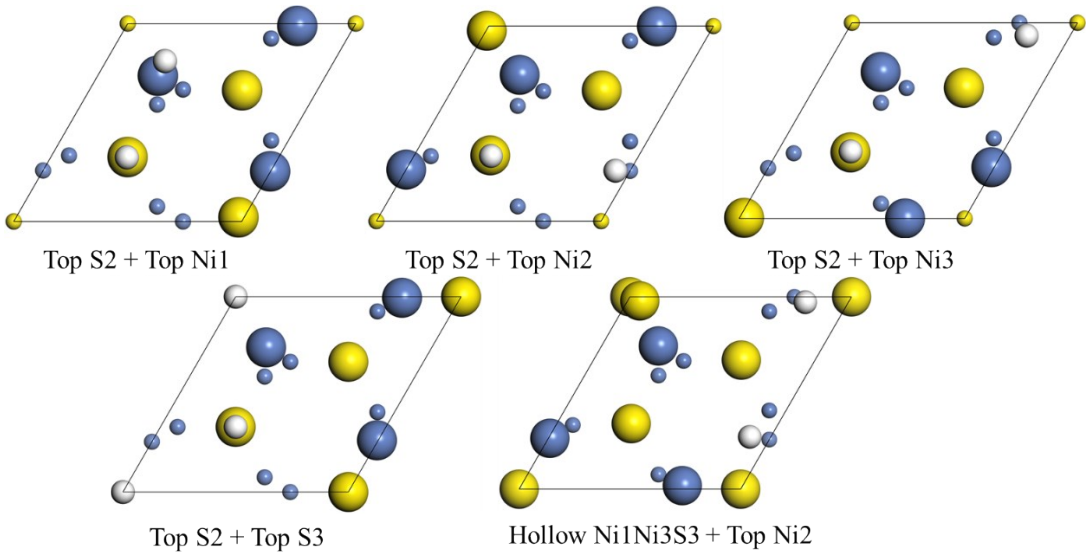

Fig. S15 The stable sites for the adsorption of two hydrogen atoms for $(^{0001})$A of Ni_3S_2 with Top S2 site or Hollow Ni1Ni3S3 site as the first hydrogen atom adsorption site.

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Table S7.**

Table S7 The details of the sites information of two hydrogen atoms for (0001)A of Ni_3S_2 with Top S2 or Hollow Ni1Ni3S3 as the first hydrogen atom adsorption site.

First site	ΔG_{H*} **(eV) (first)**	**Second site**	ΔG_{H*} **(eV) (second)**	**Preferrable HER mechanism**
Top S2	-0.143	Top Ni1	0.567	Volmer-Heyrovsky
Top S2	-0.143	Top Ni2	0.568	Volmer-Heyrovsky
Top S2	-0.143	Top Ni3	0.568	Volmer-Heyrovsky
Top S2	-0.143	Top S3	1.042	Volmer-Heyrovsky
Hollow Ni1Ni3S3	0.515	Top Ni2	0.923	Volmer-Heyrovsky

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S16.**

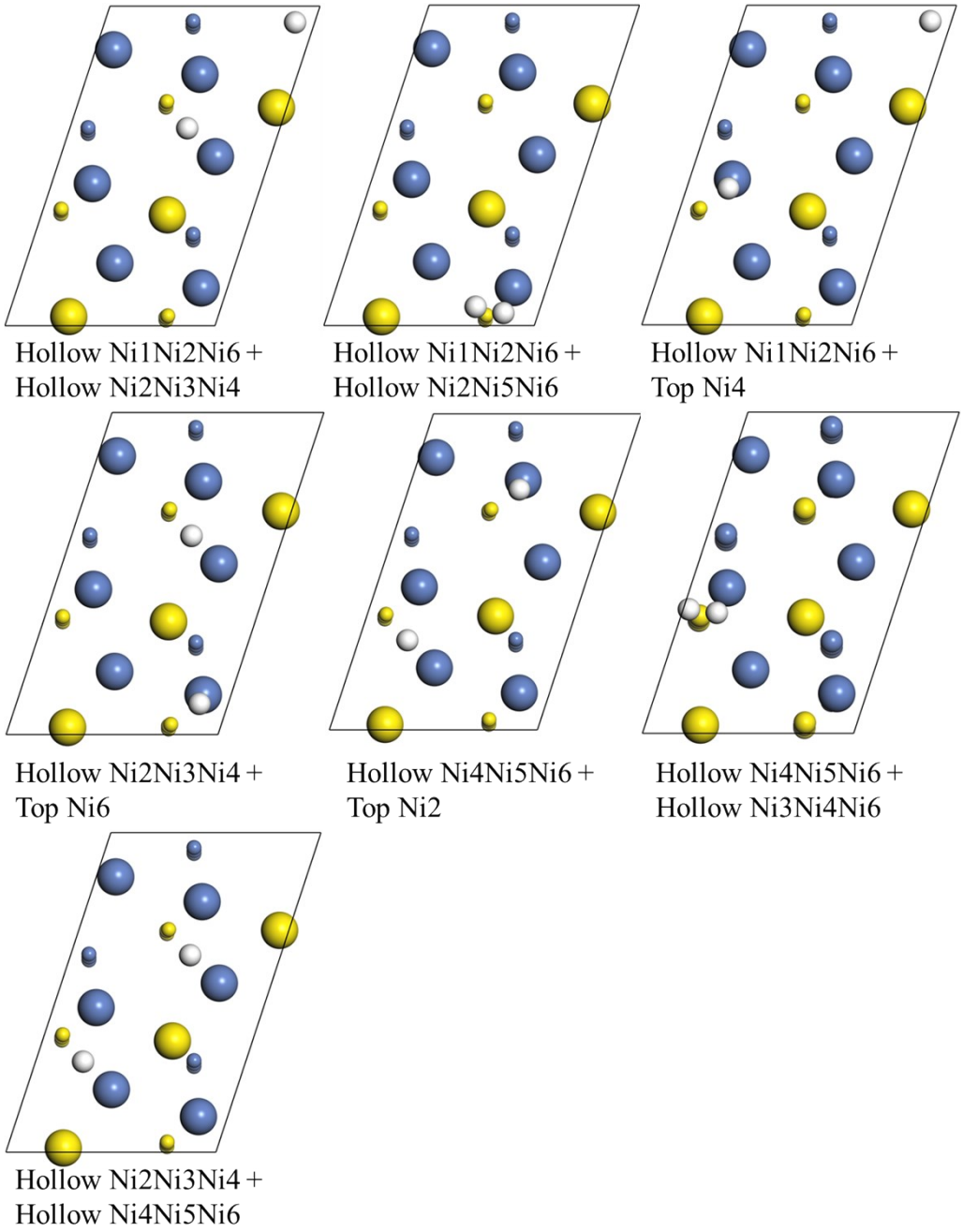

Fig. S16 The stable sites for the adsorption of two hydrogen atoms for $(10\bar{1}1)$A of Ni_3S_2 with Hollow Ni1Ni2Ni6 site, Hollow Ni2Ni3Ni4 site or Hollow Ni4Ni5Ni6 site as the first hydrogen atom adsorption site.

Table S8 The details of the sites information of two hydrogen atoms for $(10\bar{1}1)$A of Ni_3S_2 with Hollow Ni1Ni2Ni6 site, Hollow Ni2Ni3Ni4 site or Hollow Ni4Ni5Ni6 site as the first hydrogen atom adsorption site.

First site	ΔG_{H*} (eV) (first)	Second site	ΔG_{H*} (eV) (second)	Preferrable HER mechanism
Hollow Ni1Ni2Ni6	0.497	Hollow Ni2Ni3Ni4	0.587	Volmer-Heyrovsky
Hollow Ni1Ni2Ni6	0.497	Hollow Ni2Ni5Ni6	-0.252	Volmer-Tafel
Hollow Ni1Ni2Ni6	0.497	Top Ni4	0.645	Volmer-Heyrovsky
Hollow Ni2Ni3Ni4	0.498	Hollow Ni4Ni5Ni6	0.585	Volmer-Heyrovsky
Hollow Ni2Ni3Ni4	0.498	Top Ni6	0.644	Volmer-Heyrovsky
Hollow Ni4Ni5Ni6	0.499	Top Ni2	0.644	Volmer-Heyrovsky
Hollow Ni4Ni5Ni6	0.499	Hollow Ni3Ni4Ni6	-0.253	Volmer-Tafel

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S17.**

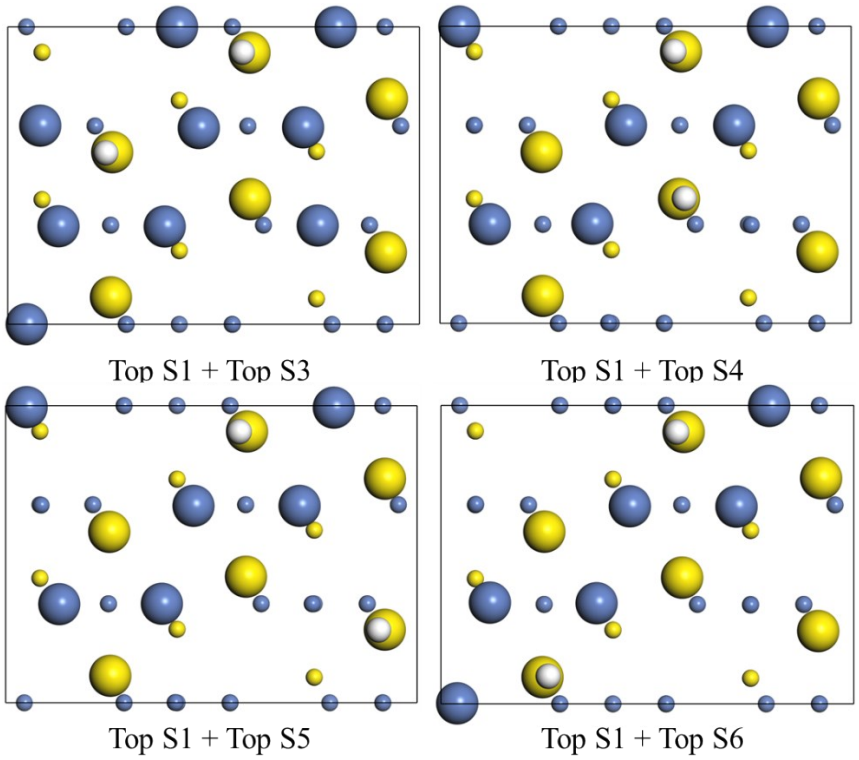

Fig. S17 The stable sites for the adsorption of two hydrogen atoms for $(11\bar{2}0)$C of Ni_3S_2 with Top S1 site as the first hydrogen atom adsorption site.

Table S9 The details of the sites information of two hydrogen atoms for $(11\bar{2}0)$C of Ni_3S_2 with Top S1 site as the first hydrogen atom adsorption site.

First site	ΔG_{H*} (eV) (first)	Second site	ΔG_{H*} (eV) (second)	Preferrable HER mechanism
Top S1	0.371	Top S3	0.460	Volmer-Heyrovsky
Top S1	0.371	Top S3	0.460	Volmer-Heyrovsky
Top S1	0.371	Top S4	0.504	Volmer-Heyrovsky
Top S1	0.371	Top S5	0.459	Volmer-Heyrovsky
Top S1	0.371	Top S6	0.521	Volmer-Heyrovsky

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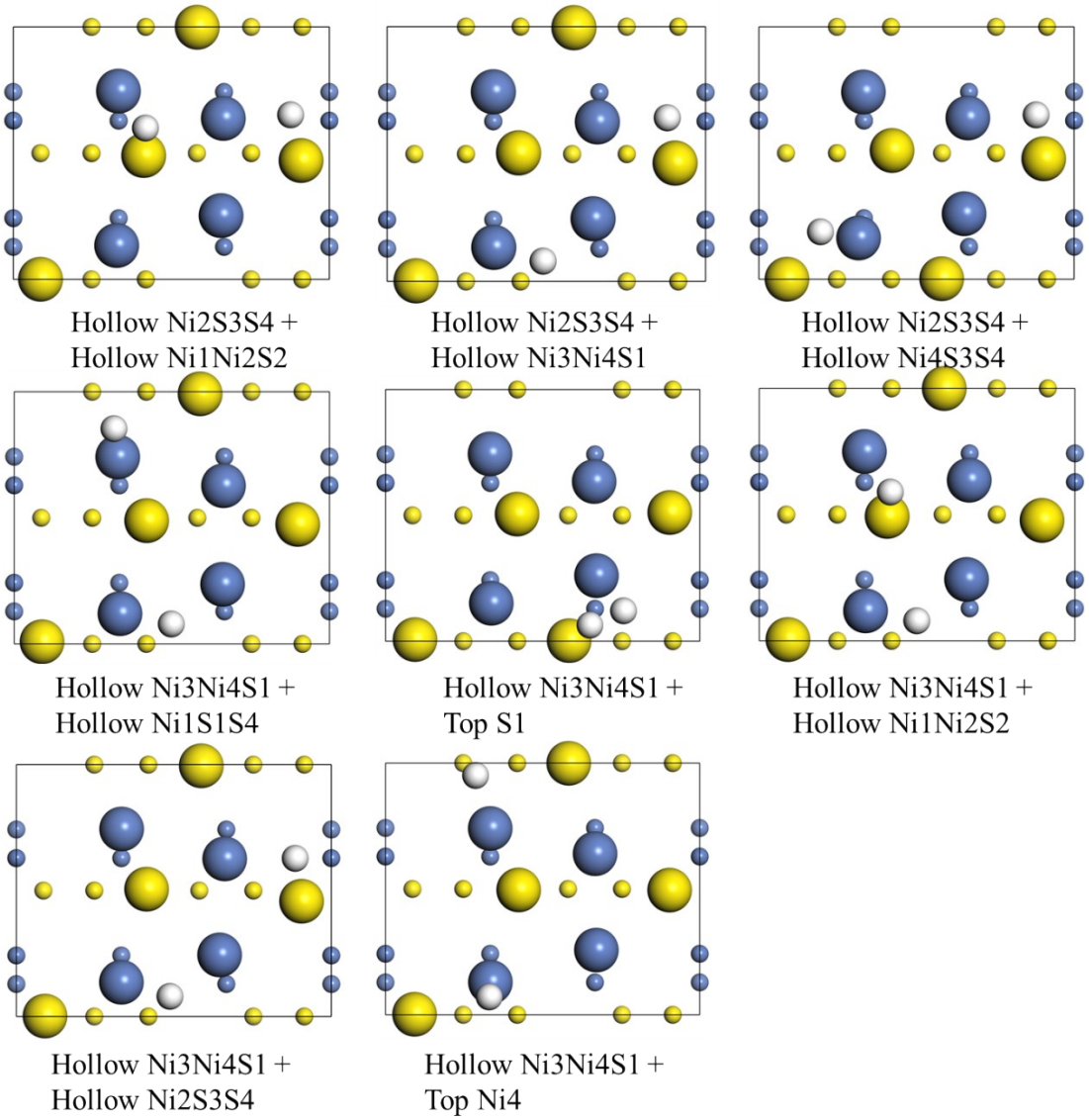

Fig. S18 The stable sites for the adsorption of two hydrogen atoms for $(10\bar{1}0)$C of Ni_3S_2 with Hollow Ni2S3S4 site or Hollow Ni3Ni4S1 site as the first hydrogen atom adsorption site.

Table S10 The details of the sites information of two hydrogen atoms for $(10\bar{1}0)$C of Ni_3S_2 with Hollow Ni2S3S4 site or Hollow Ni3Ni4S1 site as the first hydrogen atom adsorption site.

First site	ΔG_{H*} (eV) (first)	Second site	ΔG_{H*} (eV) (second)	Preferrable HER mechanism
Hollow Ni2S3S4	0.122	Hollow Ni1Ni2S2	0.637	Volmer-Heyrovsky
Hollow Ni2S3S4	0.122	Hollow Ni3Ni4S1	0.168	Volmer-Heyrovsky
Hollow Ni2S3S4	0.122	Hollow Ni4S3S4	0.563	Volmer-Heyrovsky
Hollow Ni3Ni4S1	0.254	Hollow Ni1S1S4	0.517	Volmer-Heyrovsky
Hollow Ni3Ni4S1	0.254	Top S1	0.149	Volmer-Tafel
Hollow Ni3Ni4S1	0.254	Hollow Ni1Ni2S2	0.374	Volmer-Heyrovsky
Hollow Ni3Ni4S1	0.254	Hollow Ni2S3S4	0.038	Volmer-Tafel
Hollow Ni3Ni4S1	0.254	Top Ni4	0.030	Volmer-Tafel

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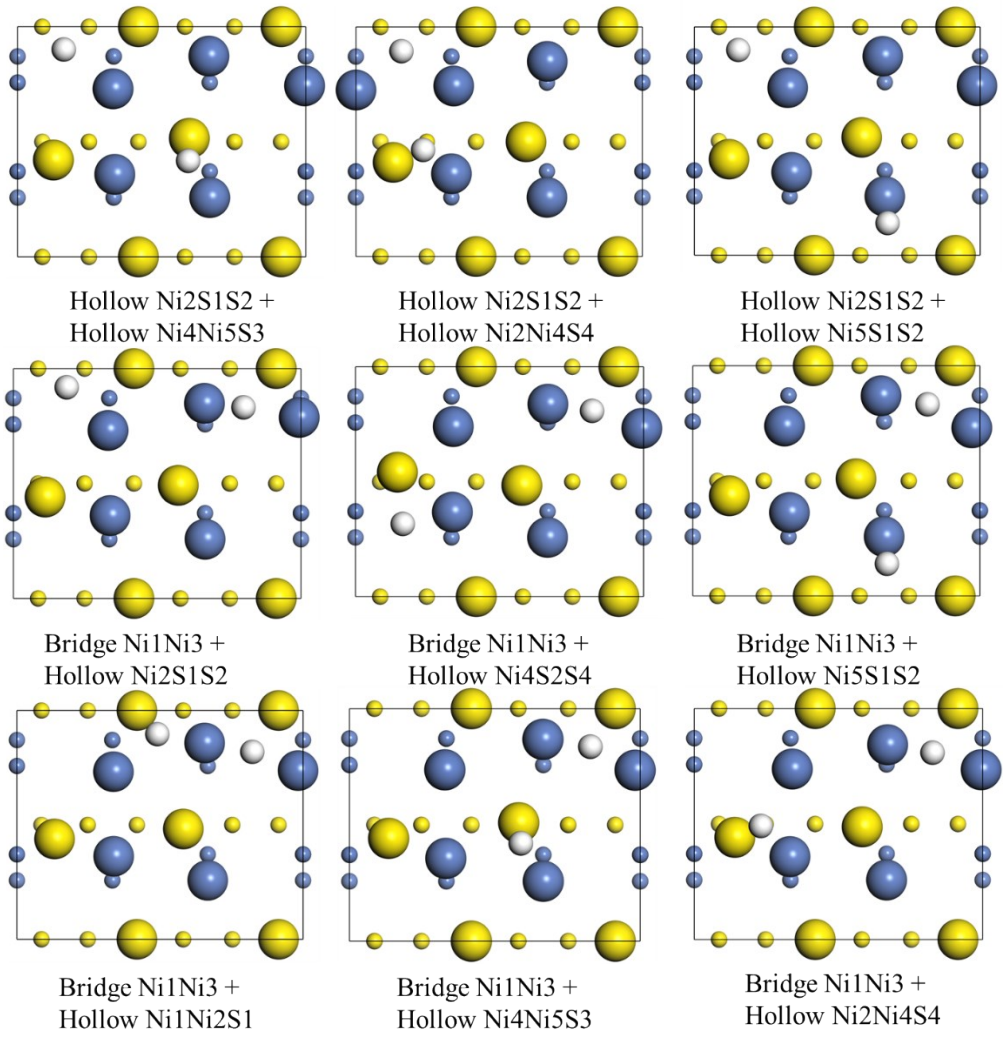

Fig. S19 The stable sites for the adsorption of two hydrogen atoms for $(10\bar{1}0)$B of Ni_3S_2 with Hollow Ni2S1S2 site or Bridge Ni1Ni3 site as the first hydrogen atom adsorption site.

Table S11 The details of the sites information of two hydrogen atoms for $(10\bar{1}0)$B of Ni_3S_2 with Hollow Ni2S1S2 site or Bridge Ni1Ni3 site as the first hydrogen atom adsorption site.

First site	ΔG_{H*} (eV) (first)	Second site	ΔG_{H*} (eV) (second)	Preferrable HER mechanism
Hollow Ni2S1S2	-0.112	Hollow Ni4Ni5S3	0.523	Volmer-Heyrovsky
Hollow Ni2S1S2	-0.112	Hollow Ni2Ni4S4	0.668	Volmer-Heyrovsky
Hollow Ni2S1S2	-0.112	Hollow Ni5S1S2	0.671	Volmer-Heyrovsky
Hollow Ni2S1S2	-0.112	Hollow Ni4Ni5S3	0.523	Volmer-Heyrovsky
Hollow Ni2S1S2	-0.112	Hollow Ni2Ni4S4	0.668	Volmer-Heyrovsky
Bridge Ni1Ni3	0.012	Hollow Ni2S1S2	-0.155	Volmer-Tafel
Bridge Ni1Ni3	0.012	Hollow Ni4S2S4	0.572	Volmer-Heyrovsky
Bridge Ni1Ni3	0.012	Hollow Ni5S1S2	0.706	Volmer-Heyrovsky
Bridge Ni1Ni3	0.012	Hollow Ni1Ni2S1	0.311	Volmer-Heyrovsky
Bridge Ni1Ni3	0.012	Hollow Ni2S1S2	-0.157	Volmer-Tafel
Bridge Ni1Ni3	0.012	Hollow Ni4Ni5S3	0.564	Volmer-Heyrovsky
Bridge Ni1Ni3	0.012	Hollow Ni2Ni4S4	0.583	Volmer-Heyrovsky

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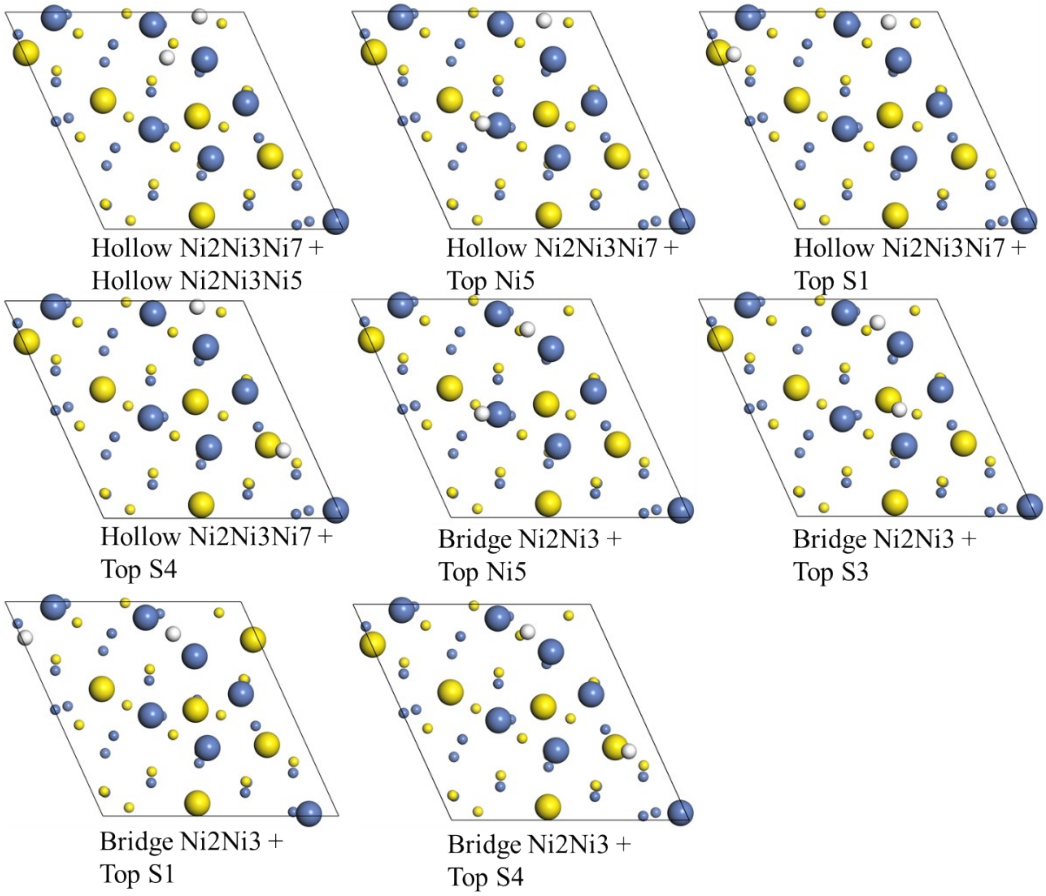

Fig. S20 The stable sites for the adsorption of two hydrogen atoms for $(11\bar{2}1)$A of Ni_3S_2 with Hollow Ni2Ni3Ni7 site or Bridge Ni2Ni3 site as the first hydrogen atom adsorption site.

Table S12 The details of the sites information of two hydrogen atoms for $(11\bar{2}1)$A of Ni_3S_2 with Hollow Ni2Ni3Ni7 site or Bridge Ni2Ni3 site as the first hydrogen atom adsorption site.

First site	ΔG_{H*} (eV) (first)	Second site	ΔG_{H*} (eV) (second)	Preferrable HER mechanism
Hollow Ni2Ni3Ni7	-0.413	Hollow Ni2Ni3Ni5	-0.036	Volmer-Heyrovsky
Hollow Ni2Ni3Ni7	-0.413	Top Ni5	0.473	Volmer-Heyrovsky
Hollow Ni2Ni3Ni7	-0.413	Top S1	0.435	Volmer-Heyrovsky
Hollow Ni2Ni3Ni7	-0.413	Top Ni5	0.530	Volmer-Heyrovsky
Hollow Ni2Ni3Ni7	-0.413	Top S4	0.472	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Hollow Ni2Ni3Ni5	-0.075	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top Ni5	0.513	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top S3	0.561	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top Ni2Ni3Ni5	-0.075	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top S1	0.292	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top Ni5	0.505	Volmer-Heyrovsky
Bridge Ni2Ni3	-0.374	Top S4	0.505	Volmer-Heyrovsky

Zhang Bo et. *Physical Chemistry Chemical Physics*. **Fig. S21.**

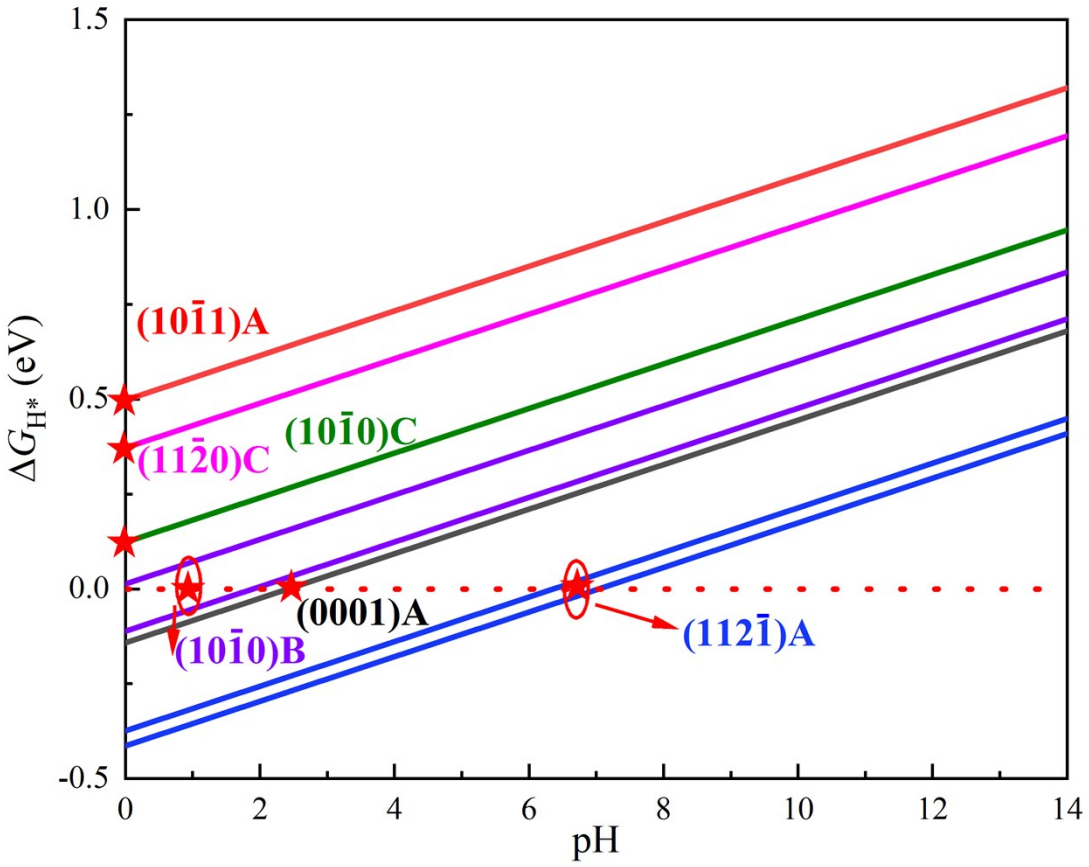

Fig. S21 The pH effect of electrolyte on the HER performance of considered six relatively stable surfaces of Ni_3S_2.

References

1. J. Hu, S. Zheng, X. Zhao, X. Yao and Z. Chen, *J. Mater. Chem. A*, 2018, **6**, 7827-7834.