1	Supplementary Information						
2	<b>Bio-inspired heterogeneous Fe<sub>4</sub>S<sub>4</sub> single-cluster catalyst for</b>						
3	enhanced electrochemical $CO_2$ reduction to $CH_4$						
4	Hengyue Xu <sup>a</sup> , Daqin Guan <sup>c</sup> and Lan Ma <sup>a,b,*</sup>						
5	<sup>a</sup> Institute of Biopharmaceutical and Health Engineering, Tsinghua Shenzhen International Graduate						
6	School, Tsinghua University, Shenzhen 518055, China.						
7	<sup>b</sup> Institute of Biomedical Health Technology and Engineering, Shenzhen Bay Laboratory, Shenzhen						
8	518055, China.						
9	<sup>c</sup> Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom,						
10	Kowloon 999077, Hong Kong, China.						
11	Corresponding authors:						
12	Lan Ma, Email: malan@sz.tsinghua.edu.cn						
13	ORCID iD: https://orcid.org/0000-0002-6610-5871						
14							
15							
16							
17							
18							
19							
20							
21							

#### 22 Binding energy

23 The adsorption energy  $E_{ads}$  for the Fe<sub>4</sub>S<sub>4</sub> cluster onto the substrate is calculated by the 24 following equation:

$$E_{ads} = E_{*Fe_4S_4} - E_{sub} - E_{Fe_4S_4} \# \# (S1)$$

where  $E_{*Fe_4S_4}$  and  $E_{sub}$  are the total energies of the substrate with and without the 26 adsorbed Fe<sub>4</sub>S<sub>4</sub> cluster, respectively.  $E_{Fe_4S_4}$  is the total energy of the isolated Fe<sub>4</sub>S<sub>4</sub> 27 cluster. In addition, for the rigor of the calculation, we considered the three most 28 common surfaces of nickel<sup>1-5</sup> Ni (100), Ni (111) and Ni (110). We calculated the 29 adsorption energies of Fe<sub>4</sub>S<sub>4</sub> cluster on Ni (100), Ni (111) and Ni (110) (Figure S1). 30 The calculation results show that the adsorption energy of Fe<sub>4</sub>S<sub>4</sub> cluster on these three 31 most common surfaces of nickel is -8.05 eV on Ni (100), -7.02 eV on Ni (111) and -32 5.72 eV on Ni (110), indicating that the Fe<sub>4</sub>S<sub>4</sub> cluster tend to adsorb on Ni (100) to form 33 the most stable supported catalysts. 34





<sup>36</sup> Figure S1. The adsorption energy of Fe4S4 cluster on Ni (100), Ni (111) and Ni

(110).

37

The adsorption energy  $E_{ads}$  for the CO<sub>2</sub> molecule onto the substrate is calculated by the following equation:

40

$$E_{ads} = E_{*CO_2} - E_{sub} - E_{CO_2} ##(S2)$$

41 where  ${}^{E} * CO_2$  and  ${}^{E} sub$  are the total energies of the substrate with and without the 42 adsorbed CO<sub>2</sub> molecule, respectively.  ${}^{E}_{CO_2}$  is the total energy of the isolated CO<sub>2</sub> 43 molecule. In addition, for the rigor of the calculation, we considered different CO<sub>2</sub> 44 adsorption patterns. As shown in **Figure S2a**, the structural model of **Figure S2a** 45 changed the molecular structure **Figure S2b** after geometric optimization. Further 46 optimization transformed into **Figure S2c** structural model. Therefore, CO<sub>2</sub> molecules 47 thermodynamically preferentially form the adsorption pattern as shown in **Figure S2c**.





50 Figure S2. Different CO<sub>2</sub> adsorption patterns on Ni100-Fe<sub>4</sub>S<sub>4</sub>.

51

## 52 Orbital properties and chemical adsorption capability

In order to further explore the catalysis origins of Ni100-Fe<sub>4</sub>S<sub>4</sub> triggered by orbital properties from a standpoint of electronic structure, we calculated the density of states and *d*-band centers of different orbitals for Ni100-Fe<sub>4</sub>S<sub>4</sub>, where the *d*-band center information can be extracted as follows:<sup>6, 7</sup>

$$\varepsilon_{d} = \int_{-\infty}^{+\infty} \rho_{d}(\varepsilon)\varepsilon d\varepsilon \Big/ \int_{-\infty}^{+\infty} \rho_{d}(\varepsilon)d\varepsilon \#(S3)$$

where  $\varepsilon_d$  is the center position of the *d* band,  $\rho_d$  is the density of state of the *d* orbital, and  $\varepsilon$  is the energy width of the *d* orbital. It has been well acknowledged that the *d*-band center closer to the Fermi level for a catalyst is often regarded to show higher chemical adsorption capability<sup>3,4</sup>.

62

57

### 63 Electrostatic potential

64 The surface properties are critical in the catalysis performance, due to the chemical 65 reactions often occur on the catalyst surface. In order to study Influence on catalyst <sup>66</sup> surface before and after CO<sub>2</sub> adsorption, we calculated the surface electrostatic potential <sup>67</sup> of the Ni100-Fe<sub>4</sub>S<sub>4</sub> and Ni100-Fe<sub>4</sub>S<sub>4</sub>-\*CO<sub>2</sub>, which can be defined as follows:<sup>8, 9</sup>

$$V_{E(r)} = \sum_{A} \frac{Z_{A}}{|R_{A} - r|} - \int \frac{\rho(r')dr}{|r' - r|} \# \#(S4)$$

68

69 where the  $V_{E(r)}$  is the molecular electrostatic potential, which is an acknowledged factor 70 for the analysis of intermolecular interactions.  $Z_A$  is the charge of the *A* atom located at 71  $R_A$  position and  $\rho(r')$  represents the charge density at r' position.

72

## 73 Work function

The work function can well evaluate the electron transport of materials, which can be
defined as follows:<sup>10, 11</sup>

$$\Phi = E_{vac} - E_F \# \# (S5)$$

<sup>77</sup> where  $\Phi$  is the work function,  $E_{vac}$  is the electrostatic potential at the vacuum level, and <sup>78</sup>  $E_F$  is the electrostatic potential at the Fermi level. In general, a lower work function <sup>79</sup> indicates that electrons are more likely to escape from the surface of the material and <sup>80</sup> indicates their easier electron transport capability.<sup>12, 13</sup>

81

### 82 Charge density difference

<sup>83</sup> The charge density difference for Ni100-Fe<sub>4</sub>S<sub>4</sub> ( $\Delta\rho$ ) and Ni100-Fe<sub>4</sub>S<sub>4</sub>-\*CO<sub>2</sub> ( $\Delta\rho$ \*) are <sup>84</sup> calculated by the following equations:<sup>14, 15</sup>

$$\Delta \rho = \rho_{Ni100 - Fe_4S_4} - \rho_{Ni100} - \rho_{Fe_4S_4} \# \# (S6)$$
  
$$\Delta \rho^* = \rho_{Ni100 - Fe_4S_4} - * co_2 - \rho_{Ni100 - Fe_4S_4} - \rho_{CO_2} \# \# (S7)$$

Where  $\rho_{Ni100-Fe_4S_4}$ ,  $\rho_{Ni100-Fe_4S_4-*CO_2}$  and  $\rho_{Ni100}$ ,  $\rho_{Ni100-Fe_4S_4}$  are the charge density of the substrate with and without the adsorbed Fe<sub>4</sub>S<sub>4</sub> cluster/CO<sub>2</sub> molecule, respectively.  $\rho_{Fe_4S_4}$ ,  $\rho_{CO_2}$  are the charge density of the adsorbed cluster/molecule.

#### 91 Bader charge analysis

92 The Bader charge<sup>16</sup> analysis for Ni100-Fe<sub>4</sub>S<sub>4</sub>-\*CO<sub>2</sub> are calculated in Table S1.
93

### 94 Reaction free energy change

<sup>95</sup> The  $\Delta$ G (reaction free energy change) for each elementary step is calculated according <sup>96</sup> to the CHE model (computational hydrogen electrode model)<sup>17, 18</sup> proposed by Nørskov <sup>97</sup> et al. by the following equation:<sup>19-21</sup>

$$_{98} \qquad \Delta G = \Delta E + \Delta E_{ZEP} - T\Delta S + eU + \Delta G_{pH} \# \# (S8)$$

where  $\Delta E$  is the reaction energy obtained from DFT calculations.  $\Delta E_{ZEP}$  and  $T\Delta S$  are 99 the zeropoint energy and entropy contributions to the reaction free energy change  $\Delta G$ , 100 respectively, which are obtained from the calculations of vibrational frequency. T is the 101 temperature, and 298.15 K is used in this system.  $\Delta S$  is the entropy change. The 102 vibrational frequencies of molecules in the gas phase are calculated in Table S3 with 103 considering GGA correct<sup>22</sup>. Table S4 present  $E_{(DFT)}$  (calculated with considering solvent 104 effect), E<sub>ZPE</sub>, TS (at 298.15 K) and G of the free molecules and the adsorbed species 105 along the almost all possible main and side reaction pathways for the Ni100-Fe<sub>4</sub>S<sub>4</sub> 106 catalyst. U and e are the electrode potential applied and the number of electrons 107 transferred, respectively.  $\Delta G_{pH}$  is the free energy correction of pH, which is calculated 108

109 as follows equation:<sup>6</sup>

$$\Delta G_{pH} = k_B T \times ln10 \times pH \# \#(S9)$$

where  $k_B$  is the Boltzmann constant. In this study, we assume that the system in acidic medium (pH = 0). The value of limiting potential ( $U_{lim}$ ) is determined by the potential determining step (PDS) with the most positive  $\Delta G$  ( $\Delta G_{max}$ ), which is calculated as follows equation:

$$U_{lim} = \Delta G_{max}/e\#\#(S10)$$

# Elementary steps in CO<sub>2</sub>RR, HER and H<sub>2</sub>SER



Figure S3. All considered pathways in the search process for the minimum energy. All the hydrogenation reactions (R1~R40) considered in the search process for the minimum energy reaction pathways of the  $CO_2$  reduction reactions (see Figure S3) can be written as:

\* 
$$+ CO_2(g) + H^+ + e^- \rightarrow OCHO * \#(R1)$$
  
\*  $+ CO_2(g) + H^+ + e^- \rightarrow COOH * \#(R2)$   
OCHO \*  $+ H^+ + e^- \rightarrow OCH2O * \#(R3)$   
OCHO \*  $+ H^+ + e^- \rightarrow OCHOH * \#(R4)$   
OCH2O \*  $+ H^+ + e^- \rightarrow OCH2OH * \#(R5)$   
OCHOH \*  $+ H^+ + e^- \rightarrow OCH2OH * \#(R6)$   
OCHOH \*  $+ H^+ + e^- \rightarrow CH2OH * \#(R6)$   
OCH2OH \*  $+ H^+ + e^- \rightarrow CHO * + H2O(1)\#(R7)$   
OCH2OH \*  $+ H^+ + e^- \rightarrow CH2O * + H2O(1)\#(R8)$   
OCH2OH \*  $+ H^+ + e^- \rightarrow CH2O(g) + * + H2O(1)\#(R9)$ 

$$CO^{*} + H^{+} + e^{-} \rightarrow COH^{*} \# (R13)$$

$$CO^{*} + H^{+} + e^{-} \rightarrow CHO^{*} \# (R14)$$

$$COH^{*} + H^{+} + e^{-} \rightarrow C + H2O(1)\# (R15)$$

$$COH^{*} + H^{+} + e^{-} \rightarrow CHOH^{*} \# (R16)$$

$$C^{*} + H^{+} + e^{-} \rightarrow CH^{*} \# (R17)$$

$$CH^{*} + H^{+} + e^{-} \rightarrow CH2^{*} \# (R18)$$

$$CH2^{*} + H^{+} + e^{-} \rightarrow CH3^{*} \# (R19)$$

$$CH3^{*} + H^{+} + e^{-} \rightarrow CH4^{*} \# (R20)$$

$$CH3^{*} + H^{+} + e^{-} \rightarrow CH4^{*} \# (R20)$$

$$CH3^{*} + H^{+} + e^{-} \rightarrow CH4^{*} \# (R21)$$

$$CH0^{*} + H^{+} + e^{-} \rightarrow CH4(g) + * \# (R21)$$

$$CH0^{*} + H^{+} + e^{-} \rightarrow CH2O^{*} \# (R23)$$

$$CH0^{*} + H^{+} + e^{-} \rightarrow CH2O(g) + * \# (R24)$$

$$CH0H^{*} + H^{+} + e^{-} \rightarrow CH2O(g) + * \# (R24)$$

$$CHOH^{*} + H^{+} + e^{-} \rightarrow CH2OH^{*} \# (R26)$$

$$CH2O^{*} + H^{+} + e^{-} \rightarrow CH2OH^{*} \# (R27)$$

$$CH2O^{*} + H^{+} + e^{-} \rightarrow CH2OH^{*} \# (R28)$$

$$CH3O^{*} + H^{+} + e^{-} \rightarrow CH4(g) + O^{*} \# (R29)$$

$$CH3O^{*} + H^{+} + e^{-} \rightarrow CH3OH^{*} \# (R30)$$

$$CH3O^{*} + H^{+} + e^{-} \rightarrow CH3OH(1) + * \# (R31)$$

OCH2OH \* + H<sup>+</sup> +  $e^- \rightarrow$  CH3OH(l) + O \* #(R10)

 $COOH * + H^{+} + e^{-} \rightarrow CO(g) + * + H2O(l)\#(R12)$ 

 $COOH * + H^{+} + e^{-} \rightarrow CO * + H2O(1) \# (R11)$ 

CH2OH \* + H<sup>+</sup> + 
$$e^- \rightarrow$$
 CH3OH \* #(R32)  
CH2OH \* + H<sup>+</sup> +  $e^- \rightarrow$  CH3OH(1) + \* #(R33)  
CH2OH \* + H<sup>+</sup> +  $e^- \rightarrow$  CH2 \* + H2O(1)#(R34)  
O \* + H<sup>+</sup> +  $e^- \rightarrow$  OH \* #(R35)  
OH \* + H<sup>+</sup> +  $e^- \rightarrow$  H2O(1) + \* #(R36)

The hydrogenation reactions (R37~R38) for HER can be written as:

\* + H<sup>+</sup> + 
$$e^- \rightarrow$$
 H \* #(R37)  
H \* + H<sup>+</sup> +  $e^- \rightarrow$  H2(g) + \* #(R38)

Hydrogen sulfide evolution reactions (R39 $\sim$ R40) for H<sub>2</sub>SER can be written as:

$$Fe4S4 * + H^{+} + e^{-} \rightarrow Fe4S3SH * \#(R39)$$

$$Fe4S3SH * + H^{+} + e^{-} \rightarrow Fe4S3 * + H2S(g)\#(R40)$$

Therefore, when U = 0 V and pH = 0,  $\Delta G$  for each elementary step (R1-R40) can be rewritten as:

$$\begin{split} \Delta G_{R1} &= \Delta G_{\rm OCHO} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{*} - \Delta G_{\rm CO_{2}(g)} \# \# (RS1) \\ \Delta G_{R2} &= \Delta G_{\rm COOH} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{*} - \Delta G_{\rm CO_{2}(g)} \# \# (RS2) \\ \Delta G_{R3} &= \Delta G_{\rm OCH2O} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{\rm OCHO} * \# \# (RS3) \\ \Delta G_{R4} &= \Delta G_{\rm OCHOH} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{\rm OCHO} * \# \# (RS4) \\ \Delta G_{R5} &= \Delta G_{\rm OCH2OH} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{\rm OCHOO} * \# \# (RS5) \\ \Delta G_{R6} &= \Delta G_{\rm OCH2OH} * - \frac{1}{2} \Delta G_{\rm H2} - \Delta G_{\rm OCHOH} * \# \# (RS6) \\ \end{bmatrix}$$

$$\begin{split} \Delta G_{R7} &= \Delta G_{CHO} * + \Delta G_{H2O(1)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{OCHOH} * \#\#(RS7) \\ \Delta G_{R8} &= \Delta G_{CH2O} * + \Delta G_{H2O(1)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{OCH2OH} * \#\#(RS8) \\ \Delta G_{R9} &= \Delta G_{CH2O(g)} + \Delta G * + \Delta G_{H2O(1)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{OCH2OH} * \#\#(RS9) \\ \Delta G_{R10} &= \Delta G_{CH3OH(1)} + \Delta G_{O} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{OCH2OH} * \#\#(RS10) \\ \Delta G_{R11} &= \Delta G_{CO} * + \Delta G_{H2O(1)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{COOH} * \#\#(RS11) \\ \Delta G_{R12} &= \Delta G_{CO(g)} + \Delta G * + \Delta G_{H2O(1)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{COOH} * \#\#(RS12) \\ \Delta G_{R13} &= \Delta G_{COH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CO} * \#\#(RS13) \\ \Delta G_{R14} &= \Delta G_{COH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CO} * \#\#(RS14) \\ \Delta G_{R15} &= \Delta G_{COH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{COH} * \#\#(RS15) \\ \Delta G_{R16} &= \Delta G_{CHOH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{COH} * \#\#(RS15) \\ \Delta G_{R17} &= \Delta G_{CH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{COH} * \#\#(RS16) \\ \Delta G_{R17} &= \Delta G_{CH2} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{COH} * \#\#(RS16) \\ \Delta G_{R18} &= \Delta G_{CH2} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH} * \#\#(RS17) \\ \Delta G_{R19} &= \Delta G_{CH2} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH} * \#\#(RS18) \\ \Delta G_{R19} &= \Delta G_{CH3} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2} * \#\#(RS19) \\ \Delta G_{R20} &= \Delta G_{CH4} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH3} * \#(RS20) \\ \Delta G_{R21} &= \Delta G_{CH4} + - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH3} * \#(RS21) \\ \end{bmatrix}$$

$$\begin{split} \Delta G_{R22} &= \Delta G_{CHOH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CHO} * \#\#(RS22) \\ \Delta G_{R23} &= \Delta G_{CH2O} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CHO} * \#\#(RS23) \\ \Delta G_{R24} &= \Delta G_{CH2O(g)} + \Delta G_{*} - \frac{1}{2} \Delta G_{H2} - \Delta G_{CHO} * \#\#(RS24) \\ \Delta G_{R25} &= \Delta G_{CH2O(g)} + \Delta G_{H2} - \frac{1}{2} \Delta G_{H2} - \Delta G_{CHOH} * \#\#(RS25) \\ \Delta G_{R25} &= \Delta G_{CH2OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CHOH} * \#\#(RS26) \\ \Delta G_{R27} &= \Delta G_{CH2OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2O} * \#\#(RS27) \\ \Delta G_{R28} &= \Delta G_{CH2OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2O} * \#\#(RS28) \\ \Delta G_{R29} &= \Delta G_{CH2OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2O} * \#\#(RS28) \\ \Delta G_{R30} &= \Delta G_{CH3OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH3O} * \#\#(RS29) \\ \Delta G_{R31} &= \Delta G_{CH3OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH3O} * \#\#(RS30) \\ \Delta G_{R32} &= \Delta G_{CH3OH} + - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2OH} * \#\#(RS31) \\ \Delta G_{R32} &= \Delta G_{CH3OH} + - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2OH} * \#\#(RS32) \\ \Delta G_{R33} &= \Delta G_{CH3OH} + - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2OH} * \#\#(RS32) \\ \Delta G_{R33} &= \Delta G_{CH3OH} + - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2OH} * \#\#(RS32) \\ \Delta G_{R34} &= \Delta G_{CH2} * + \Delta G_{H2O(I)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{CH2OH} * \#\#(RS34) \\ \Delta G_{R35} &= \Delta G_{OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{OH} * \#\#(RS35) \\ \Delta G_{R36} &= \Delta G_{OH} * - \frac{1}{2} \Delta G_{H2} - \Delta G_{OH} * \#\#(RS36) \\ {}_{S12} \\ \end{bmatrix}$$

$$\Delta G_{R37} = \Delta G_{H*} - \frac{1}{2} \Delta G_{H2} - \Delta G_{*} \# \# (RS37)$$
  
$$\Delta G_{R38} = \Delta G_{H2(g)} + \Delta G_{*} - \frac{1}{2} \Delta G_{H2} - \Delta G_{*} \# \# (RS38)$$
  
$$\Delta G_{R39} = \Delta G_{Fe4S3SH*} - \frac{1}{2} \Delta G_{H2} - \Delta G_{Fe4S4*} \# \# (RS39)$$
  
$$\Delta G_{R40} = \Delta G_{Fe4S3*} + \Delta G_{H2S(g)} - \frac{1}{2} \Delta G_{H2} - \Delta G_{Fe4S3SH*} \# \# (RS40)$$

# Geometric details in all considered CO<sub>2</sub>RR pathways

The geometry structures in all considered  $CO_2RR$  pathways are showed in Fig S3. The considered possible side reactions are showed in Fig S4.



![](_page_13_Figure_1.jpeg)

![](_page_14_Figure_0.jpeg)

Figure S5. Geometric details in considered possible side reactions.

-						
		Element	Х	Y	Z	Bader charge
	1	С	9.957	5.602	11.721	2.205007
	2	0	9.285	5.892	12.787	-1.761347
	3	0	10.988	4.721	11.812	-1.620229
	4	S	5.233	7.156	11.654	-0.950697
	5	S	3.075	5.325	14.21	-0.956829
	6	S	5.198	3.289	11.638	-0.935287
	7	S	6.784	5.06	14.509	-0.969068
	8	Fe	4.903	4.025	13.739	0.915205
	9	Fe	7.367	5.438	12.282	1.005192
	10	Fe	5.086	6.371	13.759	0.894831
	11	Fe	3.379	5.226	11.99	0.745751
	12	Ni	0	0	6.739	0.130232
	13	Ni	13.905	10.418	10.254	-0.037866
	14	Ni	1.739	1.739	6.739	0.038407
	15	Ni	1.726	1.722	10.243	-0.040476
	16	Ni	0	1.739	5	-0.046871
	17	Ni	0.001	1.736	8.507	0.060786
	18	Ni	1.739	0	5	-0.055866
	19	Ni	1.729	10.429	8.501	0.053899
	20	Ni	3.478	0	6.739	0.131261
	21	Ni	3.429	0.001	10.238	-0.044892
	22	Ni	5.216	1.739	6.739	0.064513
	23	Ni	5.222	1.615	10.305	0.135841

Table S1 Schematic diagram of the Bader charge analysis for Ni100-Fe<sub>4</sub>S<sub>4</sub>-\*CO<sub>2</sub>.

24	Ni	3.478	1.739	5	-0.062992
25	Ni	3.48	1.732	8.505	0.005502
26	Ni	5.216	0	5	-0.162944
27	Ni	5.22	0.002	8.502	-0.002634
28	Ni	6.955	0	6.739	0.137204
29	Ni	7.015	0.001	10.24	-0.01434
30	Ni	8.694	1.739	6.739	0.042819
31	Ni	8.698	1.734	10.248	-0.065877
32	Ni	6.955	1.739	5	-0.071608
33	Ni	6.955	1.745	8.519	0.036928
34	Ni	8.694	0	5	0.01099
35	Ni	8.71	0.003	8.503	0.058206
36	Ni	10.433	0	6.739	0.139561
37	Ni	10.44	0.001	10.254	-0.054062
38	Ni	12.171	1.739	6.739	0.077094
39	Ni	12.196	1.719	10.244	-0.033656
40	Ni	10.433	1.739	5	-0.115443
41	Ni	10.438	1.763	8.532	0.008241
42	Ni	12.171	0	5	-0.075836
43	Ni	12.166	10.427	8.512	0.07122
44	Ni	0	3.478	6.739	0.109293
45	Ni	0.032	3.465	10.244	-0.00927
46	Ni	1.739	5.216	6.739	0.080059
47	Ni	1.729	5.22	10.267	-0.072016
48	Ni	0	5.216	5	-0.155052
49	Ni	13.889	5.218	8.52	-0.009824
50	Ni	1.739	3.478	5	0.002789
51	Ni	1.749	3.481	8.513	-0.013389
52	Ni	3.478	3.478	6.739	0.041597
53	Ni	3.434	3.438	10.305	0.083448
54	Ni	5.216	5.216	6.739	0.0651
55	Ni	5.242	5.216	10.326	0.126554
56	Ni	3.478	5.216	5	-0.145545
57	Ni	3.484	5.217	8.519	0.028398
58	Ni	5.216	3.478	5	-0.115078
59	Ni	5.223	3.478	8.497	0.100682
60	Ni	6.955	3.478	6.739	0.00125
61	Ni	7.011	3.487	10.388	0.071652
62	Ni	8.694	5.216	6.739	0.07646
63	Ni	8.702	5.218	10.221	0.026905
64	Ni	6.955	5.216	5	-0.045407
65	Ni	6.949	5.211	8.505	0.021651
66	Ni	8.694	3.478	5	-0.009463

67	Ni	8.683	3.475	8.518	-0.01693
68	Ni	10.433	3.478	6.739	0.074054
69	Ni	10.431	3.433	10.339	0.235229
70	Ni	12.171	5.216	6.739	0.06266
71	Ni	12.238	5.235	10.342	0.250798
72	Ni	10.433	5.216	5	-0.116771
73	Ni	10.449	5.209	8.497	0.053081
74	Ni	12.171	3.478	5	-0.11328
75	Ni	12.177	3.481	8.526	0.027265
76	Ni	0	6.955	6.739	0.110035
77	Ni	0.019	6.968	10.249	-0.062765
78	Ni	1.739	8.694	6.739	0.038694
79	Ni	1.732	8.7	10.246	-0.043766
80	Ni	0	8.694	5	0.00242
81	Ni	13.905	8.69	8.511	0.034635
82	Ni	1.739	6.955	5	-0.029478
83	Ni	1.749	6.953	8.517	-0.004564
84	Ni	3.478	6.955	6.739	0.068824
85	Ni	3.452	6.994	10.305	0.079008
86	Ni	5.216	8.694	6.739	0.033721
87	Ni	5.222	8.822	10.303	0.130827
88	Ni	3.478	8.694	5	-0.07615
89	Ni	3.481	8.701	8.504	0.004754
90	Ni	5.216	6.955	5	-0.117854
91	Ni	5.221	6.955	8.492	0.046326
92	Ni	6.955	6.955	6.739	0.002149
93	Ni	6.993	6.975	10.322	0.065644
94	Ni	8.694	8.694	6.739	0.037869
95	Ni	8.709	8.7	10.244	-0.035629
96	Ni	6.955	8.694	5	-0.070451
97	Ni	6.954	8.699	8.509	0.027246
98	Ni	8.694	6.955	5	0.014765
99	Ni	8.682	6.96	8.505	0.001446
100	Ni	10.433	6.955	6.739	0.073779
101	Ni	10.401	6.937	10.311	0.125944
102	Ni	12.171	8.694	6.739	0.072245
103	Ni	12.158	8.68	10.253	-0.06149
104	Ni	10.433	8.694	5	-0.116041
105	Ni	10.434	8.683	8.516	0.02795
106	Ni	12.171	6.955	5	-0.062878
107	Ni	12.168	6.95	8.521	0.075423

**Table S2** Theoretical Limiting Potentials ( ${}^{U}_{lim}$ , V vs. RHE) and Experimental Onset Potentials ( ${}^{U}_{onset}$ , V vs. RHE) of Various CO<sub>2</sub>RR Catalysts for electrochemical CO<sub>2</sub> reduction to CH<sub>4</sub>.

Theory	U <sub>lim</sub>	Ref.	Experiments	U <sub>onset</sub>	Ref.
Ni100-Fe <sub>4</sub> S <sub>4</sub>	-0.13	This work	Cu(I)-based NNU-33	-0.50	$(2021)^{23}$
Os–N <sub>4</sub> –C SACs	-0.41	(2022) <sup>24</sup>	Graphene quantum dots	-0.48	(2017) <sup>25</sup>
Rh@P↑-In <sub>2</sub> Se <sub>3</sub>	-0.26	(2021) <sup>6</sup>	Bimetallic Cu–Pd	-0.40	(2016) <sup>26</sup>
Co@Cu	-0.87	(2019) <sup>27</sup>	Ni <sub>5</sub> Ga <sub>3</sub>	-0.50	(2016) <sup>28</sup>
Mo <sub>2</sub> C (100)	-0.56	(2016) <sup>29</sup>	Mo <sub>2</sub> C	-0.55	(2016) <sup>29</sup>
LiFeAs	-0.55	(2016) <sup>30</sup>	Cu <sub>2</sub> O-derived Cu	-0.65	(2014) <sup>31</sup>
WC (0001)	-1.00	$(2015)^{32}$	Cu foil	-0.75	$(2012)^{33}$

117 **Table S3** Total energy ( $E_{(DFT)}$ ), Zero-pint energy correction ( $E_{ZPE}$ ), entropy contribution (TS, T=298.15 K), Thermal 118 correction to  $U_{(T)}$ , Thermal correction to  $H_{(T)}$ , Entropy S, Thermal correction to  $G_{(T)}$ , GGA correct, and the Gibbs free energy 119 (G) of molecules.

	P /bar	T /K	E <sub>(DFT)</sub> /eV	E <sub>ZPE</sub> /eV	TS /eV	U <sub>(T)</sub> /eV	$H_{(T)}/eV$	S eV/K	G <sub>T</sub> /eV	GGA /eV	G /eV
CH <sub>2</sub> O	1	298.15	-21.848498	0.696103	0.676149	0.774352	0.800044	0.002268	0.123894	0.1	-21.6246
CH <sub>3</sub> OH	0.017	298.15	-30.007051	1.352811	0.843485	1.444626	1.470318	0.002478	0.626833	0	-29.38022
CH <sub>4</sub>	1	298.15	-24.062115	1.181772	0.57582	1.260042	1.285734	0.001931	0.709914	0	-23.3522
СО	1	298.15	-14.422715	0.130368	0.61089	0.194608	0.2203	0.002049	-0.390591	0.1	-14.71331
CO <sub>2</sub>	1	298.15	-22.281004	0.303653	0.662841	0.376113	0.401805	0.002223	-0.261036	0.2	-22.34204
H <sub>2</sub>	1	298.15	-6.9889204	0.270267	0.402182	0.334497	0.360188	0.001349	-0.041993	0	-7.030913
H <sub>2</sub> O	0.035	298.15	-14.148595	0.567182	0.670673	0.644347	0.670039	0.001961	-0.000634	0	-14.14923
H <sub>2</sub> S	1	298.15	-11.243708	0.404405	0.187439	0.478913	0.478913	0.000629	0.291474	0	-10.95223

120

he reaction pathway on Ni100-Fe <sub>4</sub> S <sub>4</sub> , where $*$ represents the adsorption site.						
	E <sub>(DFT)</sub> /eV	$E_{ZPE}/eV$	TS /eV	G /eV		
Ni100-Fe <sub>4</sub> S <sub>4</sub>	-531.2418589	0	0	-531.241859		
Ni100-Fe <sub>4</sub> S <sub>4</sub> -*CO <sub>2</sub>	-554.0869436	0.28196	0.152794	-553.957778		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*COOH	-557.83592	0.604326	0.150747	-557.382341		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*OCHO	-557.78531	0.620231	0.183812	-557.348891		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*OCH <sub>2</sub> O	-561.414249	0.933775	0.142283	-560.6228		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*OCHOH	-561.30432	0.930738	0.183587	-560.557169		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*OCH <sub>2</sub> OH	-565.21582	1.234317	0.192827	-564.17433		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CO	-547.06465	0.175395	0.110282	-546.999537		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*COH	-550.24517	0.480576	0.119301	-549.883895		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CHO	-550.73843	0.461147	0.105057	-550.38234		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*C	-539.9700911	0.087461	0.030558	-539.913188		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH	-542.9182097	0.347095	0.084878	-542.655993		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>2</sub>	-547.374572	0.638045	0.034211	-546.770738		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>3</sub>	-551.1642125	0.901583	0.110837	-550.373467		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>4</sub>	-555.5431035	1.204381	0.208394	-554.5471		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CHOH	-553.9445131	0.781616	0.134173	-553.29707		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>2</sub> O	-554.36187	0.715889	0.141246	-553.787227		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>2</sub> OH	-557.6455409	1.048206	0.095517	-556.692852		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>3</sub> O	-558.1354279	1.094161	0.180811	-557.222078		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*CH <sub>3</sub> OH	-561.8956823	1.41473	0.188581	-560.669533		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*O	-537.8752535	0.083164	0.035992	-537.828081		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*OH	-542.1744387	0.358436	0.082675	-541.898678		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*H (S)	-534.19866	0.190534	0.031308	-534.039434		
Ni100- Fe <sub>4</sub> S <sub>4</sub> -*H (Fe)	-534.11191	0.164842	0.023719	-533.970787		

122 Table S4 Zero-pint energy correction ( $E_{ZPE}$ ), entropy contribution (TS, T=298.15 K),

123 total energy  $(E_{(DFT)})$ , and the Gibbs free energy (G) of molecules and adsorbates along

Ni100- Fe <sub>4</sub> S <sub>4</sub> -*H (Fe-Ni)	-535.04014	0.159223	0.027	-534.907917
Ni100- $Fe_4S_4$ -*H(Ni)	-534.66971	0.112549	0.049543	-534.606704
Ni100-Fe <sub>4</sub> S <sub>3</sub> -*SH	-534.19866	0.228944	0.122264	-534.09198
Ni100-Fe <sub>4</sub> S <sub>3</sub>	-524.7112329	0	0	-524.7112329

### 125 Data availability

126 All relevant data are available from the corresponding authors on request.

#### 127 **References**

- 128 1. N. Al-Sarraf, J. T. Stuckless and D. A. King, *Nature*, 1992, **360**, 243-245.
- K. Y. Ma, L. Zhang, S. Jin, Y. Wang, S. I. Yoon, H. Hwang, J. Oh, D. S. Jeong, M. Wang, S.
   Chatterjee, G. Kim, A.-R. Jang, J. Yang, S. Ryu, H. Y. Jeong, R. S. Ruoff, M. Chhowalla, F.
   Ding and H. S. Shin, *Nature*, 2022, **606**, 88-93.
- X. Ding, L. De Rogatis, E. Vesselli, A. Baraldi, G. Comelli, R. Rosei, L. Savio, L. Vattuone, M.
   Rocca, P. Fornasiero, F. Ancilotto, A. Baldereschi and M. Peressi, *Phys. Rev. B*, 2007, 76.
- 134 4. T. Suzuki, T. Yamada and K. Itaya, J. Phys. Chem., 1996, 100, 8954-8961.
- 135 5. J. Stuckless, C. Wartnaby, N. Al-Sarraf, S. J. Dixon-Warren, M. Kovar and D. King, *J. Chem.* 136 *Phys.*, 1997, **106**, 2012-2030.
- 137 6. L. Ju, X. Tan, X. Mao, Y. Gu, S. Smith, A. Du, Z. Chen, C. Chen and L. Kou, *Nat. Commun.*,
  138 2021, 12, 5128.
- 139 7. S. Lin, Q. Wang, M. Li, Z. Hao, Y. Pan, X. Han, X. Chang, S. Huang, Z. Li and X. Ma, *ACS Catal.*, 2022, **12**, 3346-3356.
- 141 8. J. H. Stenlid and T. Brinck, J. Am. Chem. Soc., 2017, **139**, 11012-11015.
- D. Guan, J. Zhong, H. Xu, Y.-C. Huang, Z. Hu, B. Chen, Y. Zhang, M. Ni, X. Xu, W. Zhou and
  Z. Shao, *Appl. Phys. Rev.*, 2022, 9, 011422.
- M. Legesse, F. E. Mellouhi, E. T. Bentria, M. E. Madjet, T. S. Fisher, S. Kais and F. H. Alharbi, *Appl. Surf. Sci.*, 2017, **394**, 98-107.
- 146 11. Y. Wang, W. Tian, J. Wan, W. Fu, H. Zhang, Y. Li and Y. Wang, *Appl. Surf. Sci.*, 2021, 539, 147
  148312.
- 148 12. C. Kittel and P. McEuen, *Kittel's Introduction to Solid State Physics*, John Wiley & Sons, 2018.
- 149 13. N. D. Lang and W. Kohn, *Phys. Rev. B*, 1971, **3**, 1215-1223.
- 150 14. S. Tang, Q. Dang, T. Liu, S. Zhang, Z. Zhou, X. Li, X. Wang, E. Sharman, Y. Luo and J. Jiang,
   151 J. Am. Chem. Soc., 2020, 142, 19308-19315.
- 152 15. J.-C. Liu, X.-L. Ma, Y. Li, Y.-G. Wang, H. Xiao and J. Li, *Nat. Commun.*, 2018, 9, 1-9.
- 153 16. E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, J. Comput. Chem., 2007, 28, 899-908.
- 154 17. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H.
   155 Jonsson, *J. Phys. Chem. B*, 2004, **108**, 17886-17892.
- 156 18. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy Environ*.
   157 *Sci.*, 2010, **3**, 1311-1315.
- 158 19. C. Choi, S. Kwon, T. Cheng, M. Xu, P. Tieu, C. Lee, J. Cai, H. M. Lee, X. Pan, X. Duan, W. A.

- 159 Goddard and Y. Huang, *Nat. Catal.*, 2020, **3**, 804-812.
- 160 20. H. Fei, J. Dong, Y. Feng, C. S. Allen, C. Wan, B. Volosskiy, M. Li, Z. Zhao, Y. Wang, H. Sun,
- P. An, W. Chen, Z. Guo, C. Lee, D. Chen, I. Shakir, M. Liu, T. Hu, Y. Li, A. I. Kirkland, X.
  Duan and Y. Huang, *Nat. Catal.*, 2018, 1, 63-72.
- 163 21. J. Li, H. Huang, W. Xue, K. Sun, X. Song, C. Wu, L. Nie, Y. Li, C. Liu, Y. Pan, H.-L. Jiang, D.
   Mei and C. Zhong, *Nat. Catal.*, 2021, 4, 719-729.
- 165 22. S. Back and Y. Jung, ACS Energy Lett., 2017, 2, 969-975.
- 166 23. L. Zhang, X. X. Li, Z. L. Lang, Y. Liu, J. Liu, L. Yuan, W. Y. Lu, Y. S. Xia, L. Z. Dong, D. Q.
  167 Yuan and Y. Q. Lan, *J. Am. Chem. Soc.*, 2021, 143, 3808-3816.
- 168 24. J. Wang, M. Zheng, X. Zhao and W. Fan, ACS Catal., 2022, 12, 5441-5454.
- 169 25. J. Wu, S. Ma, J. Sun, J. I. Gold, C. Tiwary, B. Kim, L. Zhu, N. Chopra, I. N. Odeh, R. Vajtai, A.
- 170 Z. Yu, R. Luo, J. Lou, G. Ding, P. J. A. Kenis and P. M. Ajayan, *Nat. Commun.*, 2016, 7, 13869.
- S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. T. Haasch, J. I. Gold, M. Yamauchi and P. J. A.
  Kenis, *J. Am. Chem. Soc.*, 2017, **139**, 47-50.
- 173 27. Z. Zhao and G. Lu, J. Phys. Chem. C, 2019, **123**, 4380-4387.
- D. A. Torelli, S. A. Francis, J. C. Crompton, A. Javier, J. R. Thompson, B. S. Brunschwig, M.
  P. Soriaga and N. S. Lewis, *ACS Catal.*, 2016, 6, 2100-2104.
- 176 29. S. K. Kim, Y.-J. Zhang, H. Bergstrom, R. Michalsky and A. Peterson, *ACS Catal.*, 2016, 6, 2003-2013.
- 178 30. H. Shin, Y. Ha and H. Kim, J. Phys. Chem. Lett., 2016, 7, 4124-4129.
- 179 31. R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul and J. Baltrusaitis, *Phys. Chem.* 180 *Chem. Phys.*, 2014, 16, 12194-12201.
- 181 32. S. Wannakao, N. Artrith, J. Limtrakul and A. M. Kolpak, *ChemSusChem*, 2015, **8**, 2745-2751.
- 182 33. K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ. Sci.*, 2012, 5, 7050 7059.