## **Electronic Supplementary Information**

## Probing Metal/High-Entropy Perovskite Heterointerface for Efficient and Sustainable CO<sub>2</sub> Electroreduction

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Fig. S1 The microstructure of (a)oxidized SFVMNT, and (b) reduced NiFe@SFVMNT.



Fig. S2 The line scanning of the exsolved alloy particles.



Fig. S3 Gibbs free energies for the reduction reactions of oxides at 850 °C.



Fig. S4 EPR spectra of the oxidized SFVMNT and NiFe@SFVMNT.



Fig. S5 SEM images (a and c) and the corresponding particle size analyses (b and d) of the tested strips.



Fig. S6 CO production and Faraday efficiency of NiFe@SFVMNT based SOECs under different voltages.



**Fig. S7** (a-b) SEM images of the NiFe@SFVMNT cathode after CO<sub>2</sub> electrolysis, and (b-d) EDX line scan for the cell cross-section after the long-term test from electrodes to electrolytes.



Fig. S8 The TEM-EDS mapping images of SOEC cross-section after long-term test.



Fig. S9 The TEM-EDS mapping images of NiFe@SFVMNT cathode after long-term test.



Fig. S10 XPS spectra of (a) Fe 2p, (b) Ni 2p, (c) V 2p, (d) Mo 3d, (e) Ti 2p, (f) O 1s after the long-

term durability test.



**Fig. S11** (a) Schematic of exsolution process with relative energy of the slab, (b) Comparison of segregation and co-segregation energies with V, Mo and Ti.



Fig. S12 Constructed oxygen defective on NiFe@SFVMNT surfaces.



Fig. S13 The adsorption structure of  $CO_2$  on the surface of (a) SFVMNT and (b) NiFe@SFVMNT.



Fig. S14 Adsorption configuration of reaction intermediates on NiFe@SFVMNT surface for

CO<sub>2</sub>RR.



**Fig. S15** The Bader charges comparison of metal atoms on the surface (001) of perovskite before (a) and after CO<sub>2</sub> adsorption (b).



Fig. S16 Electron localization function (ELF) for the CO<sub>2</sub>-adsorbed on the (101) surface of SFVMNT (left) and NiFe@SFVMNT (right).



Fig. S17 (a) TPOS and (b) other elements POS diagrams.

Element	Oxidized valence	Ionic radius (nm)	χ
Sr	+2	0.144	1
Fe	+3	0.078	1.8
V	+5	0.054	1.6
Мо	+6	0.062	1.8
Ni	+2	0.072	1.9
Ti	+4	0.0605	1.5
0	-2	0.140	3.5

Table S1 Ionic radius and electronegativity of NiFe@SFVMNT sample.

Sample	Element	Element content (mol)	Atomic content (%)
	Sr	0.4403	44.77
	Fe	0.0974	9.91
NiFe@SFVMNT	V	0.0968	9.84
-	Mo	0.1036	10.53
	Ni	0.1029	10.46
	Ti	0.1425	14.49

 Table S2 ICP measurement of NiFe@SFVMNT sample.

	Space group	a (Å)	b (Å)	c (Å)	<b>R</b> <sub>p</sub> (%)	<b>R</b> <sub>exp</sub> (%)	χ <sup>2</sup>
NiFe@	NiFe: Fm-3m	3.905	3.905	3.905	10.9	5.57	6.89
SFVMNT	SFVMNT: <i>Pm-3m</i>						

Table S3 Lattice parameters of NiFe@SFVMNT derived from XRD Rietveld refinement.

	<a-0></a-0>			<b-o></b-o>			<abe></abe>
SFVMNT	<sr-o></sr-o>	<fe-o></fe-o>	<v-0></v-0>	<mo-o></mo-o>	<ni-o></ni-o>	<ti-o></ti-o>	
(kJ mol <sup>-1</sup> )	-75.43	-36.04	-57.45	-64.56	-27.58	-89.5	-350.56

Table S4 Average bonding energy of metal-oxygen for SFVMNT samples.

	Oxidized SFVMNT	NiFe@SFVMNT
Fe <sup>0</sup> (at.%)	0	20.47
Fe <sup>2+</sup> (at.%)	62.30	60.06
Fe <sup>3+</sup> (at.%)	37.70	19.47
Average valence of Fe	2.37	1.79
Ni <sup>0</sup> (at.%)	0	22.90
Ni <sup>2+</sup> (at.%)	100	77.10
Average valence of Ni	2	1.54
V <sup>4+</sup> (at.%)	0	52.31
V <sup>5+</sup> (at.%)	100	47.69
Average valence of V	5	4.52
Mo <sup>4+</sup> (at.%)	0	7.45
Mo <sup>5+</sup> (at.%)	0	15.36
Mo <sup>6+</sup> (at.%)	100	77.19
Average valence of Mo	6	5.70
Ti <sup>3+</sup> (at.%)	0	25.32
Ti <sup>4+</sup> (at.%)	100	74.68
Average valence of Ti	4	3.75

Table S5 XPS analysis of oxidized SFVMNT and reduced NiFe@SFVMNT.

	5	1		
Cathode	Feeding gas	Electrolyte/anode	Current density (A·cm <sup>-2</sup> )	Refs
$FeNi_3@La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ -GDC	pure CO <sub>2</sub>	LSGM/LSFN-GDC	~0.65	1
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$	pure CO <sub>2</sub>	LSGM/LSCF-SDC	0.71	2
$FeNi_3 @Sr_2Fe_{1.35}Mo_{0.45}Ni_{0.2}O_{6-\delta}-GDC$	95% CO <sub>2</sub> /N <sub>2</sub>	LSGM/LSCF-GDC	~0.90	3
$FeNi_3@(PrBa)_{0.95}Fe_{1.6}Ni_{0.2}Nb_{0.2}O_{5+\delta}$	pure CO <sub>2</sub>	LSGM/LSCF	~1.00	4
$CoFe@Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}-GDC$	3:7 CO: CO <sub>2</sub>	YSZ/ LSCF-GDC	1.01	5
$CoFe@Sr_2Fe_{1.35}Mo_{0.45}Co_{0.2}O_{6-\delta}-GDC$	95% CO <sub>2</sub> /N <sub>2</sub>	LSGM/BSCF-GDC	~1.05	6
$NiFe@Sr_{1.97}Fe_{1.5}Mo_{0.5}Ni_{0.1}O_{6-\delta}$	7:3 CO: CO <sub>2</sub>	LSGM/LSCF-SDC	~1.08	7
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ -SDC	pure CO <sub>2</sub>	LSGM/LSCF-SDC	1.09	2
$Cu@Sr_{0.975}Ti_{0.7}Cu_{0.2}Mo_{0.1}O_{3-\delta}$	pure CO <sub>2</sub>	LSGM/LSCF	~1.10	8

metal or alloy nanoparticles.

Table S6 Comparison of current densities for CO2 electrolysis obtained at 800 °C and 1.5 V using SFM-based cathodes and typical ceramic cathodes modified with

CoFe@La <sub>0.4</sub> Sr <sub>0.6</sub> Co <sub>0.2</sub> Fe <sub>0.7</sub> Mo	0.1O <sub>3-δ</sub> -GDC	95% CO <sub>2</sub> /N <sub>2</sub>	LSGM/BSCF-GDC	~1.20	9
$Sr_2Fe_{1.4}Mn_{0.1}Mo_{0.5}O_{6-\delta}$	-SDC	pure CO <sub>2</sub>	LSGM/LSCF-SDC	1.35	10
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}F$	0.1	pure CO <sub>2</sub>	LSGM/LSCF-SDC	1.36	11
$Sr_{2}Fe_{1.3}Cu_{0.2}Mo_{0.5}O$	6-δ	pure CO <sub>2</sub>	LSGM/LSCF-GDC	1.45	12
NiFe@La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.8</sub> M	n <sub>0.2</sub> O <sub>3</sub>	99% CO <sub>2</sub> /CO	LSGM/BLC	~1.60	13
$RuFe@Sr_2Fe_{1.4}Ru_{0.1}Mo_{0.5}G$	D <sub>6-ð</sub> -GDC	95% CO <sub>2</sub> /N <sub>2</sub>	LSGM/BSCF-GDC	~1.87	14
$NiFe@Sr_2Fe_{0.4}V_{0.4}Mo_{0.4}Ni_{$	<sub>0.4</sub> Ti <sub>0.6</sub> O <sub>3-δ</sub>	99% CO <sub>2</sub> /CO	LSGM/PBSCF-GDC	1.66	This work

Cathode	Current density	Stability	Refs
	(A cm <sup>-2</sup> )	(h)	
FeNi3@Sr2Fe1.35Mo0.45Ni0.2O6-&-GDC	~0.90	40	3
$La_{0.6}Sr_{0.4}Fe_{0.9}W_{0.1}O_{3\text{-}\delta\text{-}GDC}$	1.48	50	15
$Ru\text{-}Pr_{0.4}Sr_{0.6}Fe_{0.8}Ru_{0.1}Mo_{0.1}O_{3\text{-}\delta\text{-}}SDC$	0.90	60	16
$Sr_{2}Fe_{1.5}Mo_{0.3}Cu_{0.2}O_{6-\delta}$ -GDC	~2.20	80	17
$CoFe@La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}\text{-}GDC$	~1.20	100	9
$Sr_2FeMo_{2/3}Mg_{1/3}O_{6\text{-}\delta}$	1.40	100	18
$Sr_2Fe_{1.3}Zr_{0.2}Mo_{0.5}O_{6-\delta}$	~0.75	120	19
$Sr_{1.9}Fe_{1.5}Mo_{0.4}Ni_{0.1}O_{6\text{-}\delta}F_{0.1}\text{-}SDC$	2.66	140	20
$Sr_2(Fe_{1.0}Ti_{0.25}Cr_{0.25}Mn_{0.25}Mo_{0.25})O_{6-\delta}$	1.50	160	21
$F_{0.1}$ -La_{0.5}Sr_{0.5}FeO_{6-\delta}	2.58	200	22
$NiFe@Sr_2Fe_{0.4}V_{0.4}Mo_{0.4}Ni_{0.4}Ti_{0.6}O_{3-\delta}$	1.66	200	This work

Table S7 Comparison of long-term stability at 800  $^{\circ}\mathrm{C}$  and 1.5 V with reported typical cathodes.

Element	Before absorption	After absorption
Fel	1.46	1.54
Fe2	1.84	1.09
V1	1.56	1.77
Mo1	1.57	2.19
Ni1	1.09	1.06
Ni2	1.13	-0.03
Ti1	2.29	2.20
Ti2	2.07	1.99
Ti3	1.67	1.94

Table S8 The Bader charges comparison of metal atoms on the surface (001) of perovskite before

and after CO<sub>2</sub> adsorption.

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