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# Supporting Information

## High-entropy atomic environment converts inactive to active site for electrocatalysis

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## **1. Experimental Section**

## **1.1 Chemicals**

Polyvinylpyrrolidone (PAN), FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, and Mn(Ac)<sub>2</sub>, dimethylformamide (DMF), KOH are purchased from Sigma-Aldrich. All chemicals are used without further purification. The water used in all experiments is received by passing through an ultrapure purification system.

#### 1.2 Preparation of FeCoNiCuMn/PAN/DICY nanofiber membrane

To prepare FeCoNiCuMn/PAN/DICY nanofiber membrane, in a typical procedure, 1 mmol FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, Mn(Ac)<sub>2</sub>, DICY are dissolved in 20 mL 15 wt% PAN/DMF solution, and then stirred vigorously at 80 centigrade for 3 hours in an oil bath to obtain a homogeneous solution. In next stage, the solution is transferred to a syringe at the tip with a stainless copper needle. The electrospinning experiment is performed in an electrostatic spinning machine with a high voltage of 21 kV and a flow rate of 0.6 mL/h. The distance between the needle and the collector is 15 cm. All experiments are operated at 40 centigrade, and ultimately, FeCoNiCuMn/PAN/DICY nanofiber membrane is required.

## 1.3 Preparation of FeCoNiCuMn HEA/CNFs

The FeCoNiCuMn HEA/CNFs is prepared via homemade CVD furnace. As described in pervious report, the precursor FeCoNiCuMn/PAN/DICY nanofiber membrane are cut into 2 cm  $\times$  3 cm rectangle and placed in a ceramic boat in the central region of furnace. Then the precursor is heated to 473 K in the air at a heating rate of 20 K min<sup>-1</sup> and kept at this temperature for 10 h. After this pre-oxidation period, the furnace continued to be heated up to 1273 K at a heating rate of 20 K min<sup>-1</sup> and the temperature is constant for 10 h. After the furnance cooling down to room temperature at a rate of 20 K min<sup>-1</sup>, the HEA/CNFs is obtained.

#### **1.4 Characterization**

Field emission scanning electron microscopy (FE-SEM) is conducted on JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. Transmission electron microscopy (TEM) (AC-TEM) images are taken with JSM-2100 transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Aberration corrected scanning transmission electron microscopy (HR-ACSTEM) images and STEM-EDX mapping is carried out on modified FEI Themis TEM with a HAADF detector operated at an accelerating voltage of 300 kV. X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are prepared as described previously. Fe, Co and Ni K-edge absorption spectra (EXAFS) are performed on the beamline 1W1B at Beijing Synchrotron Radiation Facility (BSRF). The storage ring is operated at electron energy of 2.5 GeV with a beam current of 250 mA. The radiation is monochromatized by a Si (111) doublecrystal monochromator. Fe, Co, Ni foil, FeO, CoO and FeO are used as reference samples and measured in the fluorescence mode. The operando electrochemical Raman test was carried out in a round home-made electrolyzer. Ag/AgCl electrode and Pt wire served as the RE and CE, respectively. The prepared electrocatalysts were dispersed on the glass carbon electrode (GCE). The electrochemical processes were conducted in 1.0 M KOH saturated with Ar and controlled by a CHI660E electrochemical workstation. Raman spectrometer (inVia) used the laser wavelength of 785 nm.

## **1.5 Electrochemical measurements**

A three-electrode system is used to carry out the electrochemical measurements. The HEA/CNFs is cut into 1 cm × 1 cm square and directly served as working electrode. A saturated calomel electrode (SCE) and a carbon rod are used as the reference electrode (RE) and counter electrode (CE), respectively. All tests are carried out with 95% ohmic potential drop (iR) drop compensation. The iR compensation was made directly by the CHI electrochemical workstation, with the iR values probed automatically by the electrochemical

workstation. The polarization curves of HER and OER are performed from 0 V to -0.4 V vs. RHE and from 1.0 V and 2.0 V vs. RHE in 1.0 M KOH solution. Tafel plots, electrochemical surface areas (ECSA), electrochemical impedance spectroscopy (EIS) and i-t curve are performed. The turnover frequency (s<sup>-1</sup>) is calculated via the following equation: TOF=J×N<sub>A</sub>/aFn. Here, J is the current density at a given potential, N<sub>A</sub> is Avogadro number, F is Faraday constant, a is the number of electron transfer (a=2 in the HER process and a=4 in the OER process) and n is the number of active sites. The calculations of ECSA were based on the previously reported literature (Thomas Jaramillo et al., J. Am. Chem. Soc. 2015, 137, 4347–4357). For ECSA measurement, cyclic voltammetry (CV) curves at different scan rates from 10 to 50 mV s<sup>-1</sup> in the range of 1.07-1.17 V vs. RHE are conducted. The capacitive currents (Ja-Jc)/2 at 1.12 V vs. RHE as a function of scan rate were measured in order to extract doublelayer capacitance ( $C_{dl}$ ) of the electrodes:  $i_c = vC_{dl}$ . Where  $i_e$  represents the capacitive current, v is the scan rate. Meanwhile, C<sub>dl</sub> serves as an estimate of the ECSA of the solid-liquid interface as the relative ECSA is proportional to C<sub>dl</sub>. The ECSA values were calculated based on the following equation: ECSA= $C_{dl}/C_s$ . Here,  $C_s=0.04$  mF cm<sup>-2</sup>. The accelerated durability tests are performed at room temperature in 1 M KOH solution by applying the cyclic voltammetry (CV) between 1.2 V to 1.6 V vs. RHE at a sweep rate of 100 mV s<sup>-1</sup> for 2000 cycles. For overall water splitting, electrochemical measurements are performed via two-electrode system where the HEA/CNFs worked as both cathode and anode. The polarization curve is performed between 1.2 V and 1.8 V.

## **1.6 DFT calculations**

We have employed the first-principles<sup>1,2</sup> to perform all spin-polarization density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)<sup>3</sup> formulation. We have chosen the projected augmented wave (PAW) potentials<sup>4,5</sup> to describe the ionic cores and take valence electrons into account using a

plane wave basis set with a kinetic energy cutoff of 450 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than  $10^{-6}$  eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å<sup>-1</sup>. Finally, the adsorption energies (E<sub>ads</sub>) were calculated as:

 $E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$ 

where  $E_{ad/sub}$ ,  $E_{ad}$ , and  $E_{sub}$  are the total energies of the optimized adsorbate/substrate system, the adsorbate in the gas phase, and the clean substrate, respectively. The free energies of elemental reaction steps were calculated by the computational hydrogen electrode model developed by Nørskov et al. The free energy ( $\Delta G$ ) for elemental reaction step were calculated as:

$$\Delta G = \Delta \mathbf{E} + \Delta \mathbf{E} \mathbf{Z} \mathbf{P} \mathbf{E} - \mathbf{T} \Delta \mathbf{S}$$

where  $\Delta E$  is the difference between the total energy,  $\Delta EZPE$  and  $\Delta S$  are the differences in the zero-point energy and the change of entropy, T is the temperature (T =300 K in this work), respectively.

## References

Sample	$\Delta S_{mix}$
Mn-HEA/CNFs	1.66 R

Table S1. calculated configurational entropy of mixing of FeCoNiCuMn HEA/CNFs.

The calculation of mixed entropy forHEA/CNFs could be made following the equation:

 $\Delta S_{mix} = -R \Sigma_{i=1}^{n} X_{i} \ln X_{i}$ 

Where  $\Delta S_{mix}$  is the configurational entropy of mixing, R is the gas constant, X<sub>i</sub> is the molar ratio of component i, and n is the total number of elements involved.



Figure S1. Chemical structure model of the FCC phase of FeCoNiCuMn HEA.



Figure S2. Charge density difference analysis of FeCoNiCuMn/CNFs catalysts.



Figure S3. FE-SEM images of electrospun FeCoNiCuMn/PAN precursor nanofiber membranes.



Figure S4. Photographs of the FeCoNiCuMn/PAN precursor nanofiber membranes.



Figure S5. Low magnification SEM image of the FeCoNiCuMn HEA/CNFs.



Figure S6. Size distribution of FeCoNiCuMn HEA nanoparticles supported on CNFs



Figure S7. Low magnification TEM image of the FeCoNiCuMn HEA/CNFs.



**Figure S8.** High magnification TEM images of 9 randomly selected FeCoNiCuMn HEA@carbon (a-i). Sale bar: 10 nm.



**Figure S9.** (a) HAADF-STEM image, (b) EDX line-scanning elemental profile and (c) low magnification STEM-EDS mapping images of FeCoNiCuMn HEA/CNFs.



Figure S10. C 1s spectra of FeCoNiCuMn HEA/CNFs.



Figure S11. Raman spectrum of FeCoNiCuMn HEA/CNFs.



**Figure S12**. The experimental K-edge XANES spectra of Fe (a), Co (b), and Ni (c) of FeCoNiCuMn HEA/CNFs, respectively. Insets in Figure a-c are the corresponding magnified spectra.



**Figure S13.** The corresponding first derivative curves of (a) Fe, (b) Co and (c) Ni. The sample is FeCoNiCuMn HEA/CNFs.



Figure S14. Photographs of the FeCoNiCuMn HEA/CNFs electrode.



**Figure S15.** Polarization curves of Co/CNFs, Ni/CNFs and Pt/C in 1.0 M KOH solution for HER.



**Figure S16**. Tafe plots (a) and Tafel slope values (b) of FeCoNi/CNFs, FeCoNiMn/CNFs, FeCoNiCu/CNFs, FeCoNiCu/Mn/CNFs and Pt/C for alkanline HER.



**Figure S17**. CVs of (a) FeCoNi/CNFs, (b) FeCoNiMn/CNFs, (c) FeCoNiCu/CNFs and (d) FeCoNiCu/Mn/CNFs in 1.0 M KOH solution.



**Figure S18**. C<sub>dl</sub> values (a) and the corresponding electrochemical surface area (ECSA) (b) of FeCoNi/CNFs, FeCoNiMn/CNFs, FeCoNiCu/CNFs and FeCoNiCuMn HEA/CNFs.



**Figure S19.** Polarization curves of Co/CNFs, Ni/CNFs and IrO<sub>2</sub>/C in 1.0 M KOH solution for OER.



**Figure S20**. Tafe plots (a) and Tafel slope values (b) of FeCoNi/CNFs, FeCoNiMn/CNFs, FeCoNiCu /CNFs and FeCoNiCuMn /CNFs for OER.



**Figure S21**. Electrochemical impedance spectroscopy (EIS) measurement of various electrocatalysts in 1.0 M KOH solution.



Figure S22. The TOF value of FeCoNiCuMn HEA/CNFs for HER and OER.



**Figure S23**. The TOF value of FeCoNi/CNFs, FeCoNiMn/CNFs, FeCoNiCu/CNFs and FeCoNiCu/Mn HEA/CNFs for HER.



**Figure S24**. The TOF value of FeCoNi/CNFs, FeCoNiMn/CNFs, FeCoNiCu/CNFs and FeCoNiCu/Mn HEA/CNFs for OER.



**Figure S25**. The comparison in current density (1.7 V) of our as-prepared HEA/CNFs with other reported catalysts in alkaline electrolyte for overall water splitting<sup>[1-12]</sup>.



Figure S26. Durability tests of FeCoNiCuMn HEA/CNFs for overall water splitting in 1.0 M KOH solution



**Figure S27.** (a) HAADF-STEM image, (b) EDX line-scanning elemental profile and (c) low magnification STEM-EDX mapping images of FeCoNiCuMn HEA/CNFs after OWS i-t test.





Figure S29. Reaction pathway of the alkaline HER on Fe sites in HEA NPs.



Figure S30. Reaction pathway of the alkaline HER on Co sites in HEA NPs.



Figure S31. Reaction pathway of the alkaline HER on Ni sites in HEA NPs.



Figure S32. Reaction pathway of the alkaline HER on Mn sites in HEA NPs.



Figure S33. Reaction pathway of the alkaline OER on Fe sites in HEA NPs.



Figure S34. Reaction pathway of the alkaline OER on Co sites in HEA NPs.



Figure S35. Reaction pathway of the alkaline OER on Ni sites in HEA NPs.



Figure S36. Reaction pathway of the alkaline OER on Mn sites in HEA NPs.



Figure S37. Raman spectra of pristine FeCoNiCuMn/CNFs catalyst and samples immersed in KOH solution.



**Figure S38**. In situ Raman spectra of the (a) FeCoNi/CNFs, (b) FeCoNiMn/CNFs and (c) FeCoNiCu /CNFs catalyst at various potentials during the alkaline HER process.

**Supplementary Table S2.** Comparison of the overall-water-splitting activities among different earth-abundant electrocatalysts tested in 1 M KOH. J1.7 V represents the current density at a cell voltage of 1.7 V.

Electrolyzers		$J_{1.7V}$	Reference
		$[mA cm^{-2}]$	
	FeCoNiCuMn/CNFs	131.5	Our work
Alloy	FeNiCoCrMn-G	12	Adv. Sci. 2021, 8, 2002446 <sup>6</sup>
	Co SA-NC	17.7	Adv. Funct. Mater. 2021, 31, 2009853 <sup>7</sup>
	Ni <sub>1.5</sub> Co <sub>0.5</sub> @N-CNTs	20.5	Adv. Sci. 2020, 7, 1902371 <sup>8</sup>
	Co/CNFs	22.3	Adv. Mater. 2019, 31, e1808043 <sup>9</sup>
	CoNiCuMnAl@C	71	Chem. Eng. J. 2022, 429, 132410 <sup>10</sup>
	NF@NiMoCo	60.1	J. Mater. Chem. A 2019, 7, 2156-2164 <sup>11</sup>
Sulfide	Co <sub>4</sub> S <sub>3</sub> /Mo <sub>2</sub> C-NSC	24	Appl. Catal. B: Environ. 2020, 260, 118197 <sup>12</sup>
	$Co_9S_8$ $@MoS_2$	13	RSC Adv. 2022, 12, 22931- 22938 <sup>13</sup>
	Cu-Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub>	43	Appl. Catal. B: Environ. 2021, 293, 120225 <sup>14</sup>
	Mo-Co <sub>9</sub> S <sub>8</sub> @C	19	Adv. Energy Mater. 2019, 10,1903137 <sup>15</sup>
	Mo-NiS/Ni(OH) <sub>2</sub>	32	Nano Res. 2021, 14, 3466- 3473 <sup>16</sup>
	CoMoNiS-NF	21	J. Am. Chem. Soc. 2019, 141, 10417-10430 <sup>17</sup>
	Mo-Ni <sub>3</sub> S <sub>2</sub> /Ni <sub>x</sub> Py/NF	70	Adv. Energy Mater. 2020, 10, 1903891 <sup>18</sup>
Oxide	MoO <sub>3</sub> /Ni–NiO	52	Adv. Mater. 2020, 32, e2003414 <sup>19</sup>
	Co <sub>3</sub> O <sub>4</sub> -Ag	93	Appl. Catal. B: Environ. 2021, 299, 120658 <sup>20</sup>
	NiFe <sub>2</sub> O <sub>4</sub> /VACNT	6	Carbon 2019, 145, 201-208 <sup>21</sup>
	NiS/MoO <sub>3</sub> /NF	29	Nanoscale 2020, 12, 21850- 21856 <sup>22</sup>
	CoFeO@BP	32	Angew. Chem. Int. Ed. 2020, 59, 21106-21113 <sup>23</sup>
	$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta} NR$	13	Adv. Energy Mater. 2017, 7, 1602122 <sup>24</sup>
Carbide	Co <sub>6</sub> W <sub>6</sub> C@NC	51	Small 2020, 16, e1907556 <sup>25</sup>
	Co-NC@Mo <sub>2</sub> C	11	Nano Energy 2019, 57, 746- 752 <sup>26</sup>
	Co-Mo <sub>2</sub> C@N-CNTs	16	Angew. Chem. Int. Ed. 2019, 58, 4923-4928 <sup>27</sup>
	Ni/Mo <sub>2</sub> C-NCNFs	18	Adv. Energy Mater. 2019, 9, 1803185 <sup>28</sup>

Ni <sub>3</sub> ZnC <sub>0.7</sub> /NCNT	18	Carbon 2019, 148, 496-503 <sup>29</sup>
Ni-MoC@NCNT	117	Chem. Eng. J. 2021, 406:
		$126815^{30}$
W <sub>2</sub> N/WC	34	Adv. Mater. 2020, 32,
		e1905679 <sup>31</sup>

The value is calculated from the curves shown in the literature.

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