Electronic Supplementary Information (ESI)

High-entropy wire-on-sheet nanoarray catalyst with boosted preoxidation for efficient oxygen evolution reaction

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S1. Experimental section

S1.1 Chemicals

The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

S1.2 Material synthesis

The entropy-modulated wire-on-sheet hydroxide nanoarrays were fabricated via a onepot hydrothermal approach by reacting soluble metal salts with urea. Taking the highentropy NiCoZnFeCuMnCe hydroxide wire-on-sheet nanoarray (**HE-LH-7**) as an example, equivalent amounts of $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $CeCl_3 \cdot 7H_2O$ with a total metal content of 0.45 mmol were dissolved in 30 mL of deionized water containing 3.6 mmol of urea, and stirred vigorously for 20 min to form a transparent solution. After that, a piece of nickel foam (2 × 1 cm) was ultrasonically treated in ethanol for 5 min to remove the surface organics, immersed in 1% HCl solution for 5 min to remove the oxide layer on the surface, and washed with deionized water for several times. Then, the nickel foam was placed in a 50 mL Teflon-lined stainless-steel autoclave, and the precursor solution was added. The autoclave was then sealed and maintained at 120 °C for 16 h, and then allowed to cool to room temperature. The product was rinsed with deionized water and ethanol for several times and dried under vacuum overnight.

For the synthesis of the high-entropy NiCoZnFeCuMn nanoarray (**HE-LH-6**), the high-entropy NiCoZnFeCu nanoarray (**HE-LH-5**), the medium-entropy NiCoZnFe nanoarray (**LH-4**), the medium-entropy NiCoZn nanoarray (**LH-3**), the low-entropy NiCo nanoarray (**LH-2**) and the low-entropy Ni(OH)₂ nanoarray (**LH-1**), the addition of chemicals were listed in Table S1, and the synthesis approach is as same as that of HE-LH-7.

Samples							
Reagents	LH-1	LH-2	LH-3	LH-4	HE-LH-5	HE-LH-6	HE-LH-7
[mmol]							
Ni(NO ₃) ₂ ·6H ₂ O	0.45	0.23	0.15	0.11	0.09	0.075	0.064
$Co(NO_3)_2 \cdot 6H_2O$		0.23	0.15	0.11	0.09	0.075	0.064
$Zn(NO_3)_2 \cdot 6H_2O$			0.15	0.11	0.09	0.075	0.064
Fe(NO ₃) ₃ ·9H ₂ O				0.11	0.09	0.075	0.064
$Cu(NO_3)_2 \cdot 3H_2O$					0.09	0.075	0.064
Mn(NO ₃) ₂ ·4H ₂ O						0.075	0.064
CeCl ₃ ·7H ₂ O							0.064
urea	3.6	3.6	3.6	3.6	3.6	3.6	3.6

 Table S1 Summary of the addition of chemicals for the synthesis of the entropy

 modulated nanoarray catalysts.

S1.3 Structural characterizations

The X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding elemental mapping analyses were performed on a Thermo Fischer Talos F200X TEM. The atomic ratio of metals was determined by inductively coupled plasma optical emission spectrum (ICP-OES) on a Perkin Elmer Optima 7300DV ICP emission spectroscope. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg K $\alpha = 1253.6$ eV, and the resolution level was lower than 1 atom%.

S1.4 Electrocatalytic study

All the electrochemical measurements were performed in a three-electrode system linked with an electrochemical workstation (CHI660E) at room temperature. All potentials were calibrated to a reversible hydrogen electrode (RHE) and the data are presented without iR correction. An Hg/HgO electrode was used as the reference electrode, a platinum gauze electrode ($2 \text{ cm} \times 2 \text{ cm}$, 60 mesh) was used as the counter

electrode, and the nanoarray catalyst was served as the working electrode which was fixed with an electrode holder connected by a glassy carbon plate. The cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) tests were conducted at a scan rate of 2 mV s⁻¹ in O₂-purged 1 M KOH solution. The electrochemical impedance spectroscopy (EIS) measurements were operated at variable potentials from 10^{-2} - 10^{5} Hz at 1.55 V vs. RHE. The EIS data were fitted according to the following equivalent circuit, where R_s, R_{ct} and R_{int} are the series resistance, charge-transfer resistance, and solid-electrolyte interface resistance, respectively; CPE₁ and CPE₂ correspond to the capacitances derived from the solid-electrolyte interface process and the Faradaic process.



S2. Supplementary physical and electrochemical characterizations



Fig. S1 XRD patterns of the high-entropy (HE-LH-7, HE-LH-6 and HE-LH-5), medium entropy (LH-4 and LH-3) and low-entropy counterparts (LH-2 and LH-1). (A) XRD patterns of full-angle region. (B) Magnified low-angle region of the XRD patterns shows the characteristic peaks of the layered hydroxides as highlighted.



Fig. S2 (A-C) SEM images of the high-entropy NiCoZnFeCuMnCe hydroxide wireon-sheet nanoarray (HE-LH-7).



Fig. S3 TEM images of the counterparts. (A) HE-LH-6, (B) HE-LH-5, (C) LH-4, (D) LH-3, (E) LH-2, and (F) LH-1.



Fig. S4 Original HRTEM image of HE-LH-7 in Fig. 1B without labelling of the nanowires, from which the quasi-single-crystalline wire-on-sheet nanostructure can be confirmed.



Fig. S5 ICP-OES result of HE-LH-7.



Fig. S6 XPS survey spectrum of HE-LH-7.



Fig. S7 LSV curves of the catalysts measured in 1 M KOH solution.

	η ₅₀ [mV]	j _{geo} @η _{400mV} [mA cm ⁻²]	Stability	Ref.
HE-LH-7	259*	177.6	144%@6 h 118%@72 h	this work
HE-LH-6	325*	104.3	_	this work
HE-LH-5	330*	76.6	_	this work
LH-4	290*	96.2	_	this work
LH-3	359*	70.2	_	this work
LH-2	373*	62.8	_	this work
LH-1	430*	41.2	_	this work
FeCoNiMg-LDH	290*	_	95%@60 h	1
FeCoNi-LDH	310	225.5	75%@60 h	1
FeNi-LDH	330	198.5	65%@60 h	1
CoNiMnFeMg-LH	235	—	103%@100 h 118%@2000 cycles	2
CoNiMnFe-LH	255	615.5	93%@2000 cycles	2
CoNiMn-LH	390	195.5	83%@2000 cycles	2
(FeCoNi) ₃ (FeCr)-LDH	270	_	107%@17 h	3
Ni ₃ Fe-LDH	330	_	_	3
Co ₃ Fe-LDH	300	_	_	3
ZnVNiCoFeAlRu-OH	268	_	96%@50 h	4
ZnVNiCoFeRu-OH	332	_	113%@50 h	4
ZnVNiCoFeAl-OH	355	179.5	_	4

Table S2 Comparison of the OER activity and stability. * Data were obtained from the cathodic curve to avoid the influence of the pre-oxidation peak.

ZnVRu-OH	390	134.6	_	4
ZnV-OH	500	21.5	_	4
FeCoNiCrMo-HEA	300	_	102%@120 h	5
FeCoNiMo-HEA	360	298.5	105%@40 h	5
Ag@CoCuFeMoZnAgRuO OH	290	_	50%@10000 cycles	6
Ag@CoCuFeMoZnAgOOH	300	_	_	6
CoCuFeMoZnAgOOH	320	_	_	6
CoCuFeMoZnOOH	350	148.5	_	6
FeCoNiCuZn-V ⁺ -LDH	260	_	96%@200 h	7
FeCoNiCuZn-LDH	350	198	_	7
CoCuFeMoOOH@Cu	255	—	102%@72 h	8
CoCuMoOOH@Cu	250	_	_	8
ZnCoNiFeV-LH	265	_	105%@72 h	9
ZnCoNiFeAl-LH	340	_	_	9
ZnCoNiFeCr-LH	340	125.5	_	9
ZnCoNiFeGa-LH	310	_	_	9
NiFeMnZnAlMgCo- LDH/NF	280	152.5	102%@72 h	10
NiFeMnZnAlMg-LDH/NF	390	65.5	_	10
NiFeMnZnAlCo-LDH/NF	380	112.5	_	10
CoFeNiCuCr-LH	470	45.7	_	11
Sulfurized CoFeNiCuCr-LH	410	75.8	130%@72 h	11
Defective FeCrCoNiCu LDH	445	31.5	87%@16 h	12

FeCrCoNiCu LDH	_	8.9	_	12
NiCoFeCrMo-LDH	380	76.8	_	13
NiCoFeCr-LDH	442	39.5	_	13
NiCoFe-LDH	_	17.5	_	13
1% Ce:α-Ni(OH) ₂ /NF	370	70.5	_	14
1% Ce:β-Ni(OH) ₂ /NF	550	43.5	_	14
NiFeCoMnAl-OOH	280	172.5	98%@50 h	15
NiFeCoAl-OOH	300	145.3	_	15
NiFeAl-OOH	340	102.2	_	15
RuO ₂	470	33.5	_	16
IrO ₂	480	32.5	73%@1000 cycles	17



Fig. S8 CV curves of the catalysts measured in a non-redox region for evaluating the C_{dl} values. (A) LH-1, (B) LH-2, (C) LH-3, (D) LH-4, (E) HE-LH-5, (F) HE-LH-6, (G) HE-LH-7 and (H) HE-LH-7 after stability test (HE-LH-7-ac).

The estimation of the effective active surface area was carried out according to literature.^{18, 19} Typically, cyclic voltammetry (CV) tests were conducted at various scan rates (20, 40, 60, 80, 100 mV s⁻¹) in the region of 0.9~1.0 V vs. RHE where no redox reaction occurs (Fig. S8), which can be considered as the double-layer capacitive behavior. The electrochemical double-layer capacitance (C_{dl}) was estimated by plotting the Δj (j_a - j_c) at 0.95 V vs. RHE against the scan rates, where the slope is twice C_{dl} (Fig. 3C). The resulted C_{dl} values of the catalysts are shown in Table S3.

Table S3 Summary of the electrochemical double-layer capacitance (C_{dl}) and charge-transfer resistance (R_{ct}) of the catalysts.

	R _{ct}	C _{dl}
	[Ω]	[mF cm ⁻²]
LH-1	65.1	3.00
LH-2	52.8	3.20
LH-3	29.3	3.25
LH-4	14.0	3.70
HE-LH-5	20.8	3.35
HE-LH-6	16.7	4.35
HE-LH-7	8.3	4.70
HE-LH-7-ac		6.07



Fig. S9 Comparison of the normalized activity of HE-LH-7 before and after stability test.



Fig. S10 ICP-OES result of the HE-LH-7 after long-term OER operation (HE-LH-7-ac).

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