

Electronic Supplementary Information (ESI)

Tungsten Regulate Medium-Entropy Heterostructure as a highly efficient electrocatalyst for oxygen evolution reaction

Jianliang Yuan,^{a,d} Qianglong Qi,^{a,b} Qingwen Wan,^{a,b} Jiangli Gong,^{a,d} Yue Zhang,^{a,b}
Yuebin Feng,^c Chengxu Zhang^{a*} and Jue Hu^{a,b*}

^aFaculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, China

^bKey Laboratory of Unconventional Metallurgy, Kunming University of Science and Technology, Kunming, Yunnan, China

^cFaculty of Science, Kunming University of Science and Technology, Kunming, China

^dLuXi KuoBo Precious Metals Co. Ltd., Honghe, Yunnan, China

*Corresponding authors: chxzhang@kust.edu.cn, hujue@kust.edu.cn

Experimental Section

Materials

Iron acetate tetrahydrate ($\text{Fe}(\text{CO}_2\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), N,N-dimethylformamide (DMF), 2,5-dihydroxyterephthalic acid, Pyromellitic dianhydride (KOH, AR, 90%), and ethanol (EtOH) were bought from Aladdin Reagent.

Sample Preparation

FeCoNiW MOFs were synthesized via a one-step hydrothermal method. Initially, 0.25 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.25 mmol of $\text{Fe}(\text{CO}_2\text{CH}_3)_2$, 0.25 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.25 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and 0.068 mmol of 2,5-dihydroxyterephthalic acid were dissolved in a mixture of 22.5 mL of DMF, 1.35 mL of anhydrous ethanol, and 1.35 mL of deionized water. This solution was then subjected to ultrasonication for 30 minutes to form a homogeneous mixture. Subsequently, the mixture was transferred to a hydrothermal reactor and heated to 120°C for 24 hours to allow for complete solvothermal reaction. The synthesized FeCoNiW MOFs precursor was washed with ultrapure DI water, DMF, and EtOH in sequence several times, and dried at 60 °C for 12 h. Similarly, the FeCoNi MOFs precursor was synthesized using the same procedure except that the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was not added. To obtain FeCoNi alloys and FeCoNi-W alloy/oxide heterojunctions, the obtained FeCoNi MOFs and FeCoNiW MOFs sample was pretreated at 350°C for 1 hour. Subsequently, the sample was heated to 450°C at a rate of 5°C/min under a flow of mixed H_2/Ar gas (5% H_2) and

maintained at this temperature for 2 hours.

Characterizations

The powder X-ray diffraction (XRD) patterns were recorded employing a Rigaku D/Max-2200 PC diffractometer, within the diffraction angle range of $2\theta = 5\text{-}80^\circ$, utilizing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PerkinElmer PHI 5500 XPS system, featuring a resolution of 0.3-0.5 eV, sourced from a monochromated aluminum anode with Mo K α radiation (1486.6 eV). The XPS spectra were calibrated against the C 1s peak of adventitious carbon at 284.80 eV. Field-emission scanning electron microscopy (FESEM) imaging was carried out using a Nona-Nano SEM450 at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (HAADF-STEM-EDX) were conducted on a Tecnai G2 TF30 operating at 300 kV. The electrochemical Raman measurements were carried out on a confocal LabRAM Soleil Raman Microscope Raman system (HORIBA FRANCE SAS). A He-Ne laser with 532 nm excitation wavelength and a 50 \times microscope objective with a numerical aperture of 0.55 were used in all measurements. Raman frequency was calibrated by a standard silicon (Si) wafer to 520.7 cm^{-1} during each experiment. Raman curves were recorded ranging from 50 to 2000 cm^{-1} .

Electrochemical Measurements

Electrochemical measurements of the as-synthesized samples were performed with a CHI760E electrochemistry workstation (CH Instruments, Inc.) using a standard three-electrode electrochemical cell with Pt sheet and Hg/HgO as the counter electrode and the reference electrode, respectively. 50 μL of the catalysts ink was loaded on a clean NF electrode (NF, 0.5 cm^2) by drop coating to form the electrode, and dried slowly at room temperature. The final mass loading of the catalysts on electrode is around 1 mg cm^{-2} . The electrochemical measurements were all performed at room temperature, and the potential was referenced to that of the reversible hydrogen electrode (RHE). For the RHE calibration, the potential difference between Hg/HgO and RHE was measured in 99.999% pure H_2 saturated 1.0 M KOH aqueous solution. During the measurement, high-purity H_2 is bubbled into the electrolyte to saturate the electrolyte and fix the reversible hydrogen potential. Cyclic voltammograms (CV) were taken several cycles to bubble away the surface contaminates and at the same time stabilize the catalysts. The polarization curves were obtained by linear sweeping with a scan rate of 1 mV s^{-1} in O_2 -saturated 1.0 M KOH aqueous solution. Double layer capacitance (C_{dl}) was estimated by the CV curves at various scan rates (10-50 mV) in the potential region of 0.1-0.2 V vs. RHE. All the polarization curves were iR-corrected, except as otherwise noted. Electrochemical impedance spectroscopy (EIS) is recorded at an applied

potential of 1.53 V vs. RHE from 100 kHz to 0.1 Hz. Chronopotentiometry (CP) responses curve was performed under a high constant current density of 100 mA cm⁻² in 1.0 M KOH using carbon rod as the counter electrode at room temperature.

The electrochemically active surface areas (ECSA)

It is known that the electrochemical active surface area (ECSA) of the electrocatalyst is proportional to the electrochemical double-layer capacitance (C_{dl}), which can be evaluated by measuring the scan-rate-dependent CV in the non-Faraday region. The C_{dl} value can be expressed by the equation $\Delta j = (j_a - j_c)/2$ at 1.07 V vs. RHE and the curves of different scanning rates. The electrochemical active surface area (ECSAs) of a catalyst can be calculated from the double layer capacitance (C_{dl}) according equation:

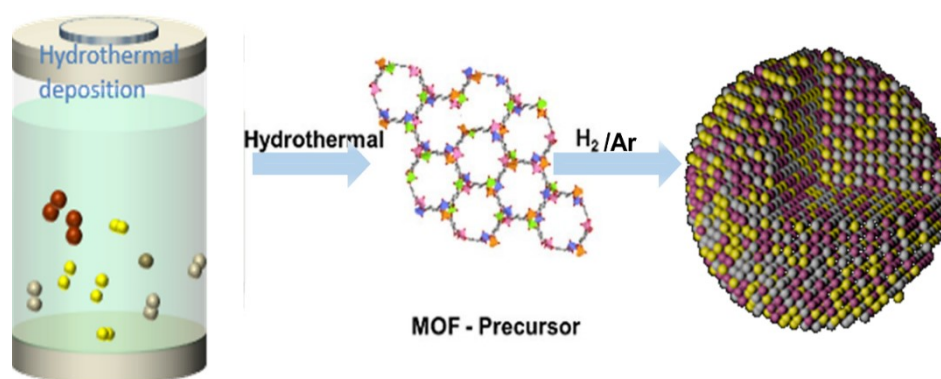
$$ECSA = \frac{C_{dl}}{C_s}$$

where C_s is the capacitance of the catalyst of an atomically smooth planar surface of material per unit area under identical electrolyte conditions. (C_s , assumed as 0.04 mF cm⁻² in 1.0 M KOH).

Turnover frequency (TOF) calculations

Turnover frequency (TOF) of the catalysts: Based on the LSV, $TOF = j \times A / (4 \times F \times m / M)$, where j is the current density (mA cm⁻²) at a given overpotential, A is the surface area of working electrode, F is the faraday constant (96485 C mol⁻¹), m are the mass loading of the catalyst, and M is the molecular weight of the catalyst unified with one active center per formula unit, respectively. All the catalytically related metal atoms were assumed to be accessible for catalysis the OER.

Supplementary Figures



Scheme S1. Synthesis schematic diagram of FeCoNi-W

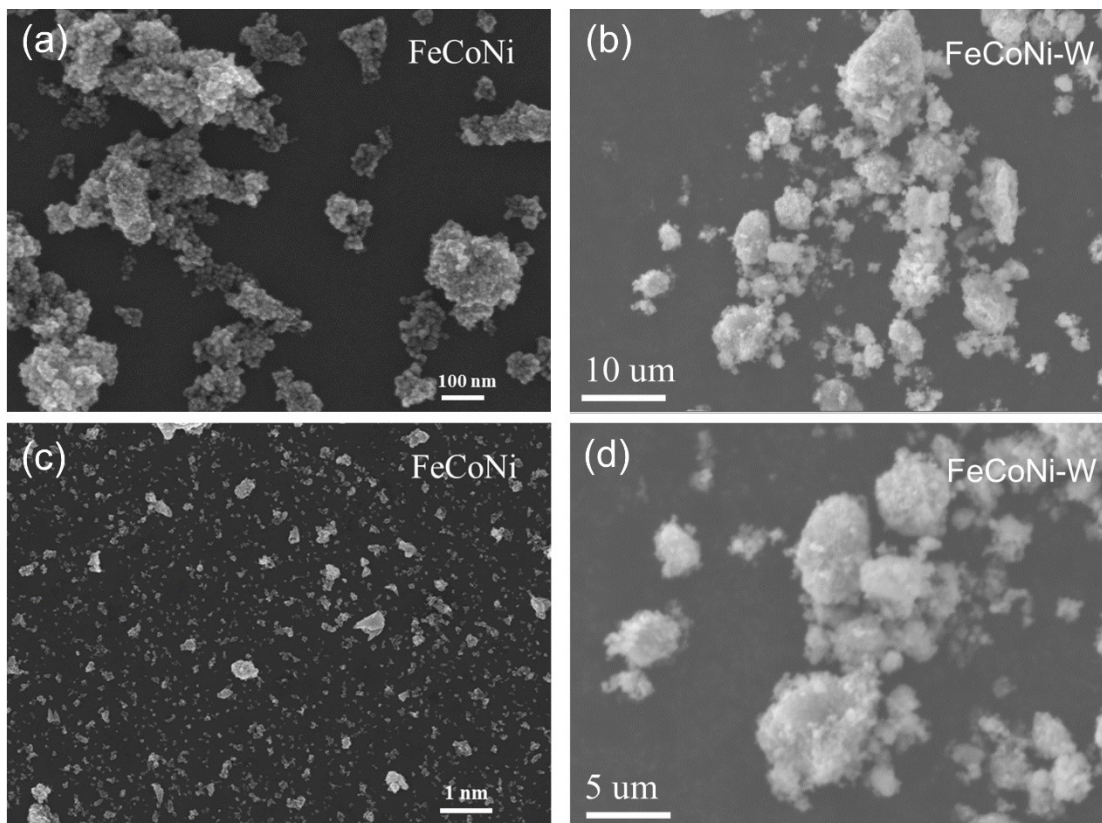


Figure S1. FESEM images of FeCoNi alloy (a, c) and FeCoNi-W (b, d)

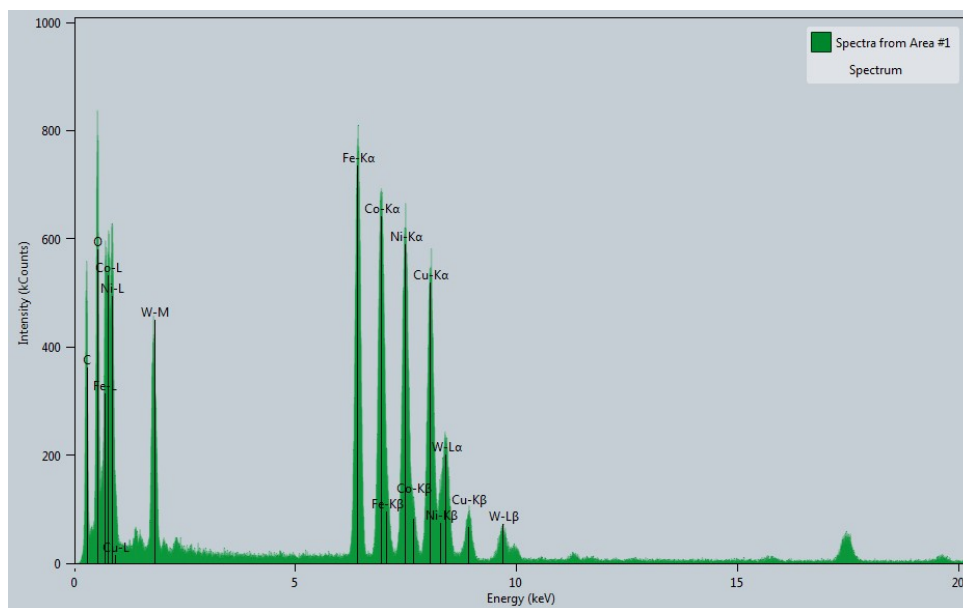


Figure S2. EDS spectra of FeCoNi-W nanoporous alloys.

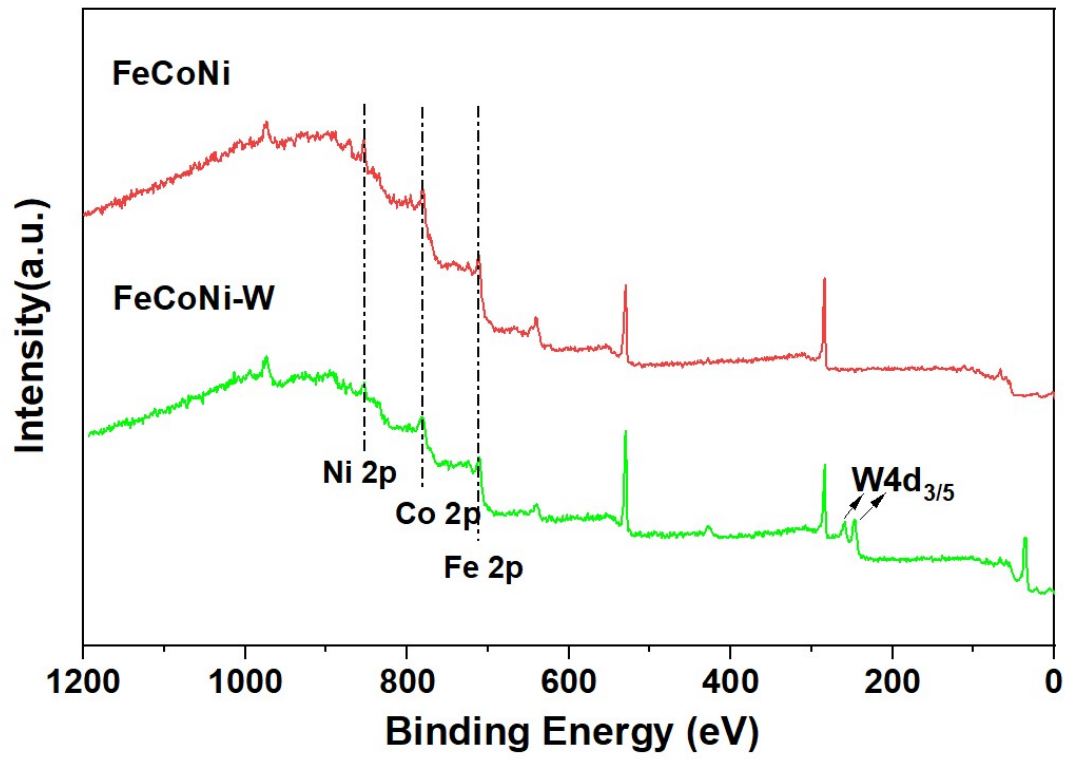


Figure S3. Survey XPS spectra of FeCoNi-W and FeCoNi.

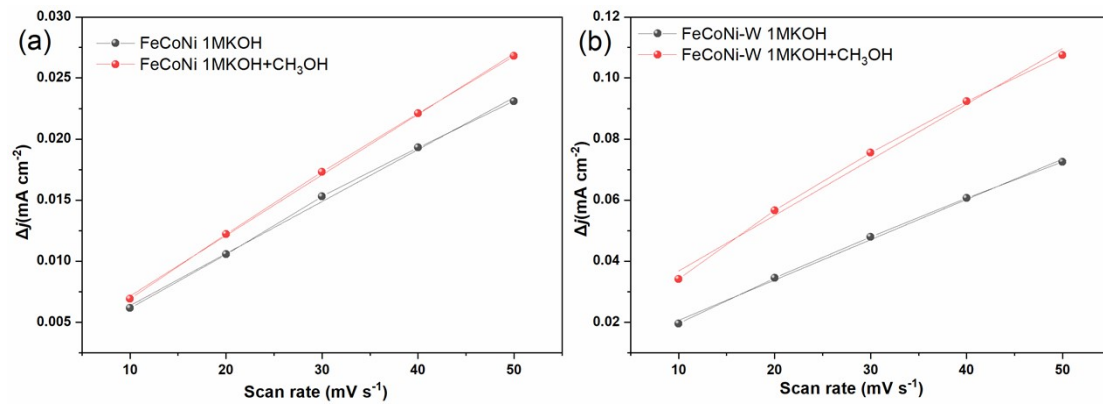


Figure S4. C_{dl} values of (a) FeCoNi and (b) FeCoNi-W in the absence and presence of methanol.

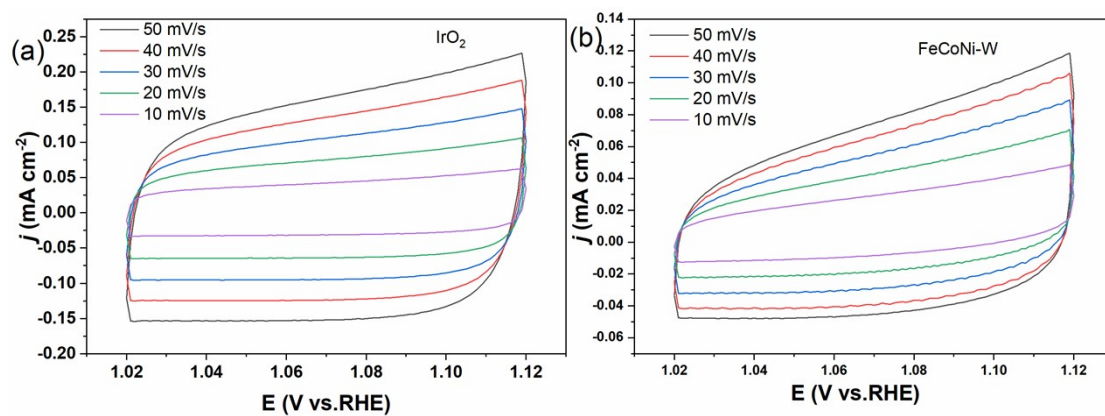


Figure S5. (a) CV curve of IrO₂ in NF at 1.0 M KOH. (b) CV curve of FeCoNi-W in NF at 1.0 M KOH.

Supplementary Tables

Table S1. Comparison of OER performance for FeCoNi-W with other recently reported transition metal-based catalysts.

Catalysts	η_{10} (mV)	Tafel (mV dec ⁻¹)	Reference
FeCoNi-W	270	43.2	This work
FeCoNi	301	71.3	This work
(CrMnFeCoNi)S	295	68	<i>Adv. Energy Mater.</i> , 2021 , 11, 2002887
FeCoNiMn@HEO	302	83.7	<i>J. Power Sources</i> 2019 , 430, 104-111.
NiMnFeMo	310	65	<i>Chem. Eng. J.</i> 2021 , 404, 126530.
FeCoNiAlTi	299	37.9	<i>Adv. Mater.</i> 2020 , 32 (21), e2000385
CoCrFeNiMn	363	61.4	<i>Journal of Materials Research and Technology</i> , 2023 , 23, 5357-5367
Co-Fe-Ga-Ni-Zn	370	71	<i>Nano Res.</i> 2021 , 15, 4799–4806
La(CrMnFe ₂ CoNi)O ₃	343	54	
La(CrMnFeCo ₂ Ni)O ₃	325	51.2	<i>Adv. Funct. Mater.</i> 2021 , 31 (27), 2101632
La(CrMn ₂ FeCoNi)O ₃	353	66.3	
La(CrMnFeCoNi)O ₃	359	78.6	
AlNiCoRuMo	270	54.5	<i>ACS Mater. Lett.</i> 2020 , 2 (12), 1698-1706.
CoFeNiMoWTe	373	40.5	<i>Adv. Energy Mater.</i> 2023 , 13, 2301420.
NiCuMnCoFe	283	81.09	<i>Rare Met.</i> 2023 , 42, 3607–3613
MnFeCoNiCu	323	85.5	<i>Nat Commun</i> 2023 , 14, 6019.
IrFeCoNiCu-HEA	302	58	<i>Nano Lett.</i> 2023 , 23, 14, 6637–6644
FeCoNiCuPd	390	96	<i>Chem. Comm.</i> , 2021 , 57, 2637-

CoNiCuMnMo	320	107.2	<i>J. Am. Chem. Soc.</i> , 2022 , 144, 7224-7235
FeCoNiMnRu/CNFs	308	61.3	<i>Nat. Commun.</i> , 2022 , 13, 2662

Table S2. The overpotentials for FeCoNi-W, FeCoNi, IrO₂ and NF substrate.

Catalysts	10 (mA cm ⁻²)	100 (mA cm ⁻²)
NF	451	676
IrO ₂	330	453
FeCoNi	290	357
FeCoNi-W	270	320