- ² Constructing medium-entropy spinel oxide FeNiMnO₄/CeO₂
- ³ heterojunction as high-performance electrocatalyst for oxygen

4 evolution reaction

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1 Text S1 Chemicals

Iron (III) chloride hexahydrate (FeCl₃·6H₂O, 99%), nickel (II) chloride hexahydrate (NiCl₂·6H₂O, 99%), and absolute alcohol (C₂H₆O, 99%) were purchased from Macklin. Manganese (II) chloride tetrahydrate (MnCl₂·4H₂O, 99%), cerous nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99%), N, N-dimethylformamide (DMF, 99%), triethylamine (TEA, 99%), sodium hydroxide (NaOH, 99%) and potassium hydroxide (KOH, 99%) were bought from Aladdin Reagent. Benzenetricarboxylic acid (C₉H₆O₆, 99%) was obtained from J&K Chemical. Nafion solution (5 wt.%) was purchased from Aldrich. All reagents were directly served as obtained without further depuration.

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10 Text S2 Synthesis

Firstly, FeCl₃·6H₂O (1 mmol), NiCl₂·6H₂O (1 mmol), MnCl₂·4H₂O (1 mmol), and 1,3,5benzenetricarboxylic acid (315.2 mg) were added to N,N-dimethylformamide (60 ml), deionized water (5 mL) and anhydrous ethanol (2.5 mL) for stirring 30 min to form a homogeneous solution. Then the mixed solution were poured into a 100 mL stainless-steel reactive kettle. The reaction temperature and time for the solvothermal method were 140 °C and 48 h, respectively. Finally, FeNiMn-MOFs were obtained by washed with ethanol for 3 times, and dried at 60 °C for 24 h. The resulting powders were collected and used as the precursors for the medium-entropy oxides.

Ce(NO₃)₃·6H₂O (100.0 mg) and NaOH (800.0 mg) were added to deionized water (70 mL) for 18 stirring 10 min. Then the FeNiMn-MOFs (200.0 mg) were added above solution for stirring 60 min. 19 Next, the mixed solution was poured into a 100 mL stainless-steel reactive kettle. The reaction 20 temperature and time for the solvothermal method were 200 °C and 24 h, respectively. Finally, 21 FeNiMnO₄/CeO₂ were obtained by washed with ethanol for 3 times, and dried at 50 °C for 24 h. For 22 comparison, FeNiMnO₄ is obtained without the addition of Ce(NO₃)₃·6H₂O, and CeO₂ is obtained 23 without the addition of FeNiMn-MOFs. As the control group, we changed the content of 24 Ce(NO₃)₃·6H₂O (50.0 mg, 100.0 mg and 150.0 mg), denoted as FeNiMnO₄/CeO₂-50, 25 FeNiMnO₄/CeO₂-100 and FeNiMnO₄/CeO₂-150. 26

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28 Text S3 Characterization

The phase composition of samples was detected by X-ray diffraction (XRD, Cu Kα, λ=1.542 Å,
Ultimate Ill). The tube voltage is 40 kV, the tube current is 40 mA, and the scan speed is 5°/min.
The morphology of samples was observed via using transmission electron microscopy (TEM, JEOL

JEM-2100F). Furthermore, the transmission electron microscope (TEM, Titan3 Cubed 60-300) 1 outfitted with a high-angle annular dark field (HAADF) detector and a spherical aberration (C_s) probe 2 corrector. The atomic level of the specimens were obtained by STEM Titan at 300 keV. Elemental 3 analysis was employed by STEM-EELS spectrum with a Gatan Quantum 966 system. The zeta 4 potential measurement was carried out using Malvern spray analyzer (Malvern Panalytical) 5 instruments. The X-ray photoelectron spectroscopy (XPS, Al Ka, Escalab-250Xi) was operated to 6 analyze the elemental composition of the samples and determine the valence state of the element. The 7 calibration standard of experimental data was 284.6 eV binding energy of C 1s peak. Raman spectral 8 experiments were performed using a 96 Raman spectrometer (Horiba LabRam) with a visible 9 wavelength of 532 nm. 10

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12 Text S4 Electrochemical measurements

Electrochemical measurements were conducted with a standard three-electrode system in the 13 electrochemical workstation (CHI 760E) at room temperature. Normally, 2 mg electrocatalyst powers 14 was dispersed in mixed solvents (0.2 mL of ethanol, 0.1 mL water and 0.02 mL Nafion solution) for 15 sonicating 1 h to obtain a homogeneous catalyst ink. Next, 20 µL catalyst suspension was applied 16 uniformly to the nickel foam electrode $(1 \times 1 \text{ cm}^2)$ each time and dry at room temperature. Repeat the 17 above process until the solution has dripped off to prepare a electrocatalyst supported nickel as 18 working electrodes. The platinum sheet and Ag/AgCl were regarded as the counter and reference 19 electrode, respectively. All potentials were calibrated to the reversible hydrogen electrode (RHE) by 20 the equation E(vs. RHE) = E(vs. Ag/AgCl) + 0.059pH + 0.197 V. The activities were appraised by 21 linear sweep voltammetry (LSV) curves with a scan speed of 5 mV s⁻¹ in 1 M KOH solution. The 22 LSV were calibrated by iR compensation (90 %). The electrochemical impedance spectroscopy (EIS) 23 was evaluated within the scope of 10⁻² to 10⁵ Hz. The electrochemical surface area (ECSA) was 24 counted by the electrochemical double-layer capacitances (C_{dl}) obtained by cyclic voltammetry (CV)25 curves.^[S1] The CV curves of electrocatalysts were recorded at different scanning rates (20, 40, 60, 80 26 and 100 mV·s⁻¹) in the non-Faraday interval. The OER stability tests were carried at room temperature 27 by potential cycling between 0 to 0.1V (Vs RHE) at a potential sweep rate of 50 mV s⁻¹ for a given 28 number of cycles. Besides, the durability of electrocatalyst was operated by the chronoamperometric 29 test. 30

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Text S5 Computational details

The static electronic correlations were taken into account within the GGA method.^[S2] The energy 3 cutoff of plane-wave basis set is 450 eV. Residual forces is less than 0.01 eV/Å. The vacuum layer 4 was set to 15 Å to avoid the interaction of periodic structures. Furthermore, the Grimme's DFT-D3 5 method is put into dispersion interaction.^[S3] The FeNiMnO₄ (311) and CeO₂ (111) crystal plane are 6 deemed as active surface to proceed out the DFT calculations. 7

For OER calculation, the four-electron pathway currently occurs in the alkaline environment in 8 accordance with the following steps: 9

$$OH^- + * \rightarrow *OH + e^- \tag{1}$$

$$*OH + OH^{-} \rightarrow *O + H_2O + e^{-}$$
(2)

$$*O + OH^{-} \rightarrow *OOH + e^{-}$$
(3)

$$*OOH + OH^{-} \rightarrow *+O_{2} + H_{2}O + e^{-}$$
(4)

The free energy difference for different OER steps is calculated as: 14

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$$\Delta G_1 = \Delta G_{*\rm OH} \tag{5}$$

$$\Delta G_2 = \Delta G_{*\rm O} - \Delta G_{*\rm OH} \tag{6}$$

$$\Delta G_3 = \Delta G_{*\rm OOH} - \Delta G_{*\rm O} \tag{7}$$

$$\Delta G_4 = 4.92 - \Delta G_{*\rm OOH} \tag{8}$$

The Gibbs free energy of OER intermediates is defined as $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$, where ΔE , 19 ΔE_{ZPE} , T and ΔS represent the reaction energy, zero-point energy, temperature (298.15 K) and the 20 entropy, respectively. 21

22
$$\Delta E_{*\rm OH} = E_{*\rm OH} - E_* - (E_{\rm H2O} - 1/2E_{\rm H2})$$
(9)

23
$$\Delta E_{*0} = E_{*0} - E_* - (E_{\rm H2O} - E_{\rm H2})$$
(10)

$$\Delta E_{*OOH} = E_{*OOH} - E_* - (2E_{H2O} - 3/2E_{H2})$$
(11)

where E_{*OH} , E_{*O} and E_{*OOH} represent the total energies of *OH, *O and *OOH species adsorption 25 on the slab, respectively. The E_* , $E_{H^{2O}}$ and E_{H^2} represent energies of slab, H_2O and H_2 , respectively. 26 27

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	$d_{11} = 0.31 \text{nm}$
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3	Figure. S1. a) TEM images of CeO ₂ . b) HRTEM images of CeO ₂ . Inset of b) are the corresponding SAED patterns.
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- 2 Figure S2. a) TEM images of FeNiMnO₄ medium-entropy oxide. b) HRTEM images of FeNiMnO₄ medium-entropy 2^{-1} with the second s
- 3 oxide. Inset of b) is the corresponding SAED patterns.









Figure S5. Crystal model of FeNiMnO₄/CeO₂ heterojunction.





2 Figurre S6. Electrostatic potential and work function distribution of a) FeNiMnO₄ and b) CeO₂. c) The energy band
3 diagrams of FeNiMnO₄ and CeO₂ before and after the formation of heterojunction.

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Figure S9. XPS survey spectra of O 1s for FeNiMnO₄/CeO₂ heterojunction.





Figure S10. The OER performances of the FeNiMnO₄/CeO₂-x in 1 M KOH. a) LSV curves. b) Tafel plots.

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2	Figure S11. Equivalent electrical circuit of electrochemical impedance spectroscopy.
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3 Figure S13. a) C_{dl} and ESCA of samples. Scan rate dependence of the current densities of b) CeO₂, c)

 $FeNiMnO_4/CeO_2$ heterojunction, d) $FeNiMnO_4$.



Figure S14. OER polarization curves of samples based on ECSA.







Figure S16. The Nyquist plots of FeNiMnO₄/CeO₂ before and after the stability test.





2 Figure S17. a) XRD of FeNiMnO₄/CeO₂ after the stability test. b) Raman spectra of FeNiMnO₄/CeO₂ before and
3 after the stability test.

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2 Figure S18. XPS spectra of a) Fe 2p, b) Ni 2p, c) Mn 2p, d) Ce 3d and e) O 1s for the FeNiMnO₄/CeO₂ after the
3 stability test

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3 Figure S19. HAADF-STEM image and corresponding elemental mapping of FeNiMnO₄/CeO₂ heterojunction after

4 24 h stability test.





2 Figure S20. Charge density difference of intermediates adsorption on the Ni sites of FeNiMnO₄/CeO₂
3 heterojunction. The depletion of electrons is shown in cyan and accumulation of electrons is drawn in yellow, and
4 the isosurface is set to 0.005 e Å⁻³.





2 Figure S21. Charge density difference of intermediates adsorption on the Ni sites of FeNiMnO₄. The depletion of

3 electrons is shown in cyan and accumulation of electrons is drawn in yellow, and the isosurface is set to 0.005 e $Å^-$

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2 Figure S23. Integral method for calculating the d-band center of Fe atoms in a) FeNiMnO₄/CeO₂ heterojunction;

- 3 b) FeNiMnO₄.
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Figure S24. Integral method for calculating the d-band center of Ni atoms in a) FeNiMnO₄/CeO₂ heterojunction; b) FeNiMnO₄.





2 Figure S25. Integral method for calculating the d-band center of Mn atoms in a) FeNiMnO₄/CeO₂ heterojunction;

- 3 b) FeNiMnO₄.
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1 Table S1. Comparison of OER performance for medium-entropy spinel oxide FeNiMnO₄/CeO₂

2 heterojunction with other medium/high-entropy electrocatalysts.

Sample	Electrolyte (KOH)	η ₁₀ /mV	Tafel slope /mV·dec ⁻¹	Ref	
FeNiMnO ₄ /CeO ₂			241	11 9	This work
heterojunction	1.0 WI KOII	271		T IIIS WUTK	
(NiFeCoMn) ₃ S ₄	1.0 M KOH	289	75.6	[S4]	
CoFeNiMnZnB	1.0 M KOH	261	57	[85]	
MnFeCoNiCu	1.0 M KOH	263	43	[S6]	
$(La_{0.6}Sr_{0.4})$	1 0 M KOH	320	45	[\$7]	
$(Co_{0.2}[FeMnNiMg]_{0.8})O_3$		520		[2,]	
(MgFeCoNiZn)O	1.0 M KOH	300	45	[S8]	
NiCoFeMnCrP	1.0 M KOH	270	52.5	[S9]	
FeCoNiMo	1.0 M KOH	250	48	[S10]	
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Ni_{0.2}Zn_{0.2})_{3}O_{4}$	1.0 M KOH	295	54	[S11]	
$(Fe_{0.2}Co_{0.2}Ni_{0.2}Cr_{0.2}Mn_{0.2})_3O_4$	1.0 M KOH	275	50.3	[S12]	
La(CrMnFeCo ₂ Ni)O ₃	1.0 M KOH	325	51.2	[S13]	

Note: $\eta 10$, overpotential at 10 mA·cm⁻².

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