

**Synergistic multi-d orbital hybridization in PtFeCoNiMnMo
nanoparticle high-entropy alloys for enhanced alkaline hydrogen
evolution**

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Configurational Entropy Calculation

The configurational entropy (ΔS_{mix}) of multi-element alloys increases with the number of different cation species¹. The formula for calculating ΔS_{mix} is expressed as follows:

$$\Delta S_{\text{mix}} = -R \sum C_i \ln C_i \quad (1)$$

Where R denotes the gas constant, and C_i represents the molar fraction of each cation species. Based on the calculated ΔS_{mix} values, alloys can be categorized into three types: low-entropy alloys ($\Delta S_{\text{mix}} < 1R$), medium-entropy alloys ($1R \leq \Delta S_{\text{mix}} \leq 1.51R$), and high-entropy alloys (HEAs, $\Delta S_{\text{mix}} > 1.51R$)^{2, 3}.

The atomic radius difference (δ) and mixing enthalpy (ΔH_{mix}) can be calculated using the following equations:

$$\delta = \frac{\sum C_i r_i}{\sqrt{\sum i C_i \left(1 - \frac{r_i}{r}\right)^2}} \quad (2)$$

$$\Delta H_{\text{mix}} = 4 \sum_{i=1}^n \sum_{j \neq i} \Omega_{ij} C_i C_j \quad (4)$$

$$(5)$$

Where r is the average atomic radius of the alloy, r_i refers to the atomic radius of the i th metal element, and $\Delta H_{ij}^{\text{mix}}$ represents the mixing enthalpy of the binary ij alloy³.

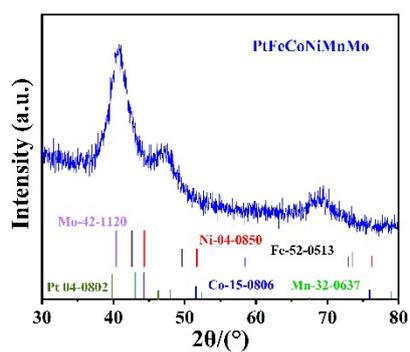
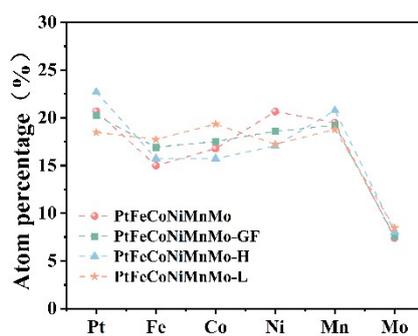


Figure S1. XRD spectrum of PtFeCoNiMnMo.



Figures S2. ICP-determined mass percentages of Pt, Fe, Co, Ni, Mn, and Mo in the catalyst.

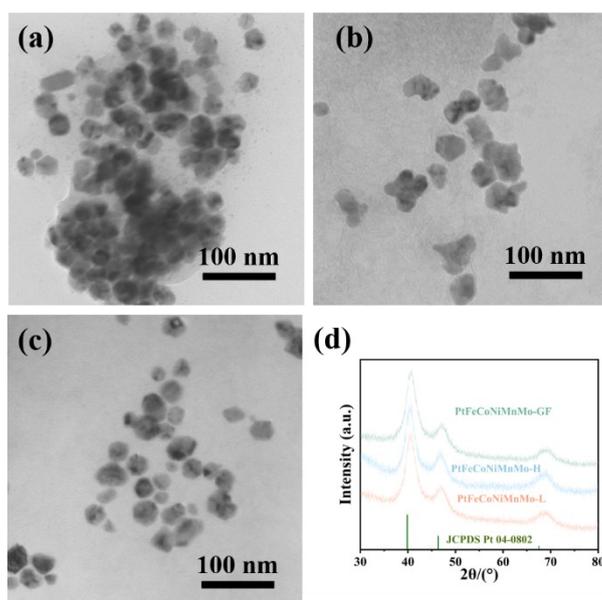


Figure S3. (a-c) TEM image, and (d) XRD spectrum of PtFeCoNiMnMo-GF, PtFeCoNiMnMo-H, and PtFeCoNiMnMo-L.

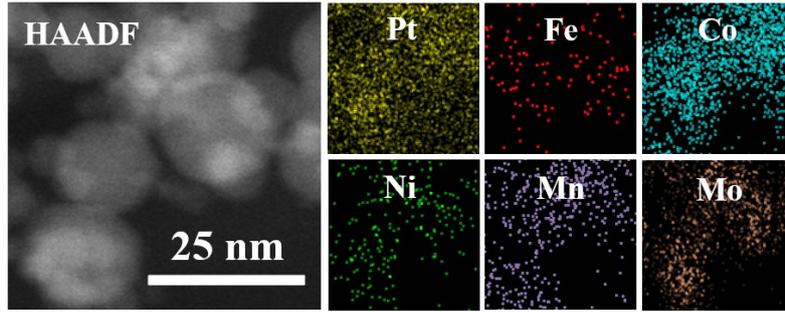


Figure S4. HAADF-STEM image PtFeCoNiMnMo with elemental mapping images for Pt, Fe, Co, Ni, Mn and Mo elements.

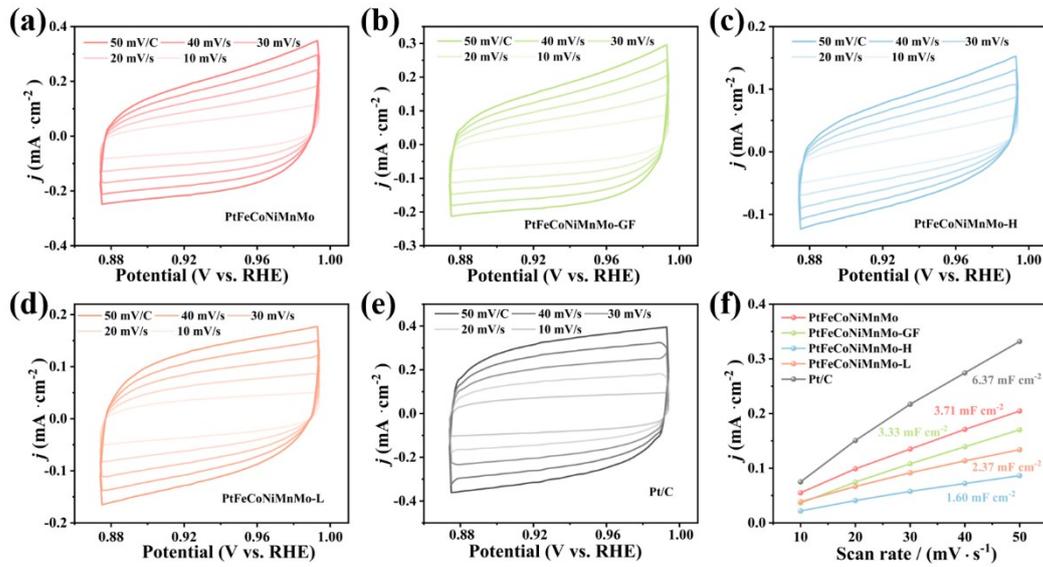


Figure S5. (a-e) CV curves of catalysts in the double layer region at scan rates of 10, 20, 30, 40 and 50 mV s $^{-1}$ in 1.0 M KOH. (f) The C_{dl} capacitance of catalysts.

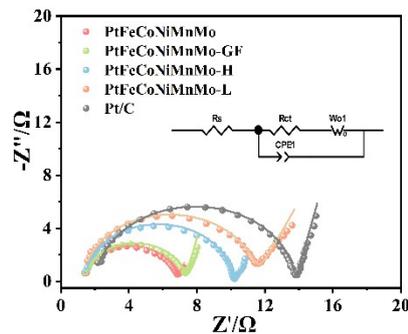


Figure S6. Nyquist plots of catalysts for HER at a potential of 0.00 V vs. RHE.

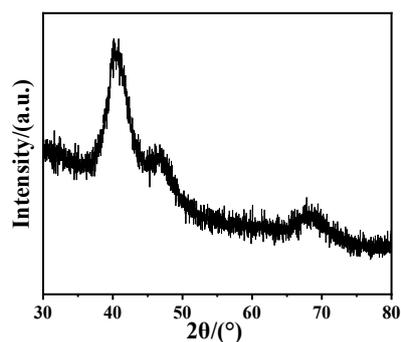


Figure S7. XRD spectrum of PtFeCoNiMnMo catalyst after more than 50 h stability of hydrogen evolution reaction.

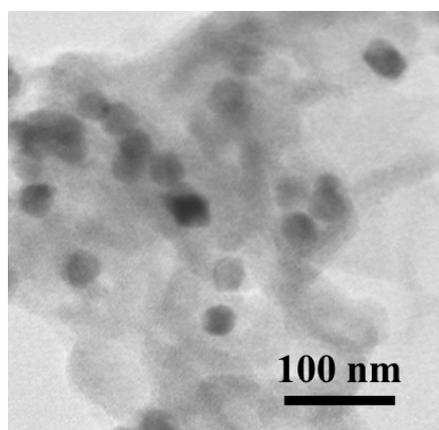


Figure S8. TEM spectrum of PtFeCoNiMnMo catalyst after more than 50 h stability of hydrogen evolution reaction.

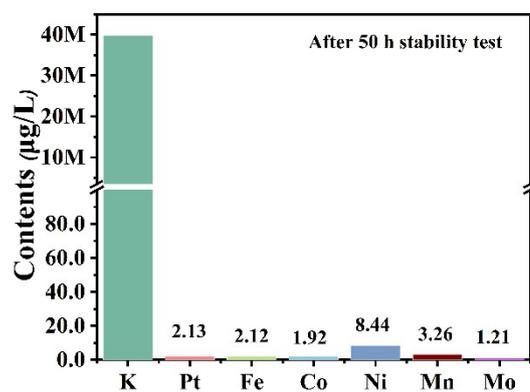


Fig.S9 The ICP-OES results of PtFeCoNiMnMo catalyst after 50 h stability test confirm that only trace elements are dissolved.

Table S1. ICP-OES results of the contents of Pt, Fe, Co, Ni, Mn, and Mo in HEA (wt%, normalized to 100% for metallic components).

Catalyst	Elements (Wt%)					
	Pt	Fe	Co	Ni	Mn	Mo
PtFeCoNiMnMo	45.58	9.46	11.16	13.70	12.09	8.01
PtFeCoNiMnMo-GF	44.91	10.74	11.74	12.40	12.00	8.22
PtFeCoNiMnMo-H	48.40	9.60	10.13	10.94	12.47	8.46
PtFeCoNiMnMo-L	41.96	11.54	13.27	11.78	12.01	9.44

Table S2. ICP-OES results of the contents of Pt, Fe, Co, Ni, Mn, and Mo in HEA.

Catalysts	Elements (atomic rate%)					
	Pt	Fe	Co	Ni	Mn	Mo
PtFeCoNiMnMo	20.69	14.99	16.77	20.66	17.49	19.49
PtFeCoNiMnMo-GF	20.25	16.91	17.53	18.58	16.53	19.20
PtFeCoNiMnMo-H	22.69	15.73	15.72	17.05	18.05	20.76
PtFeCoNiMnMo-L	18.47	17.74	19.34	17.23	18.44	18.78

Table S3. The mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), and atomic radius difference of each alloy.

Catalysts	ΔH_{mix} (kJ·mol ⁻¹)	ΔS_{mix} (J·K ⁻¹ ·mol ⁻²)	δ
PtFeCoNiMnMo	-8.41	14.52	3.29
PtFeCoNiMnMo-GF	-8.44	14.58	3.26
PtFeCoNiMnMo-H	-8.71	14.54	3.30
PtFeCoNiMnMo-L	-8.34	14.65	3.33

Table S4. Results of three parallel ICP-OES tests on PtFeCoNiMnMo catalysts (wt%, normalized to 100% for metallic components).

Number	Elements (wt%)					
	Pt	Fe	Co	Ni	Mn	Mo
1	44.96	9.41	11.30	13.86	12.38	8.08
2	45.39	9.21	11.22	13.79	11.89	8.49
3	45.56	9.34	11.04	13.78	11.97	8.31

Table S5. The double-layer capacitance (C_{dl}), the electrochemically active surface area (ECSA) difference of each catalyst.

Catalysts	C_{dl} (mF cm ⁻²)	ECSA (m ² /g)
PtFeCoNiMnMo	3.71	92.75
PtFeCoNiMnMo-GF	3.33	83.25
PtFeCoNiMnMo-H	1.60	40.00
PtFeCoNiMnMo-L	2.37	59.25
Pt/C	6.37	159.25

Table S6. Corresponding parameter of EIS for HER. The parameter of R_s , R_{ct} , and W_o for the electrocatalysts for HER.

Catalysts	R_s (Ω)	R_{ct} (Ω)	W_o (Ω)
PtFeCoNiMnMo	0.63	5.39	0.0012
PtFeCoNiMnMo-GF	0.66	5.95	0.0004
PtFeCoNiMnMo-H	0.82	8.63	0.0051
PtFeCoNiMnMo-L	1.54	10.11	0.0006
Pt/C	1.39	11.75	0.0022

Table S7. Comparison of HER performance of PtFeCoNiMnMo electrocatalyst with recently reported catalysts.

materials	Electrolyte	η_{10}	Tafel slope	Ref.
		(10 mA cm^{-2})	(mV dec^{-1})	
PtFeCoNiMnMo	1.0 M KOH	21	47.06	This work
PtNiCuMnMo	1.0 M KOH	21	74	4
FeCoNiMnRu	1.0 M KOH	37	44	5
$\text{Ni}_3\text{ZnC}_{0.7}@/\text{NiPt}_1/\text{NPC}$	1.0 M KOH	23	28.45	6
$\text{Pt}_{58}\text{Cu}_{15}\text{Ni}_{27}$	1.0 M KOH	30	40	7
$\text{Pt}_{26}\text{Ir}_7\text{Fe}_{13}\text{Co}_{22}\text{Ni}_{32}\text{NF}$	1.0 M KOH	26	44.5	8
$\text{FeCoNiCrPt}@/\text{Pt}$	1.0 M KOH	51	52.9	9
PtNiMg	1.0 M KOH	22	30.9	10
$\text{PtFeCoNiCuCr}@/\text{HCS}$	1.0 M KOH	29	39.24	11
$(\text{FeCoNiB}_{0.75})_{97}\text{Pt}_3$	1.0 M KOH	27	/	12
IrPdPtRhRu	1.0 M KOH	16	31	13
PtPdRhRuCu	1.0 M KOH	10	87	14
FeCoNiCuPd	1.0 M KOH	29.7	47.2	15

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