

## Supporting Information

### **Noble-metal high-entropy-alloy tuning the products of electrocatalytic 5-hydroxymethylfurfural oxidation**

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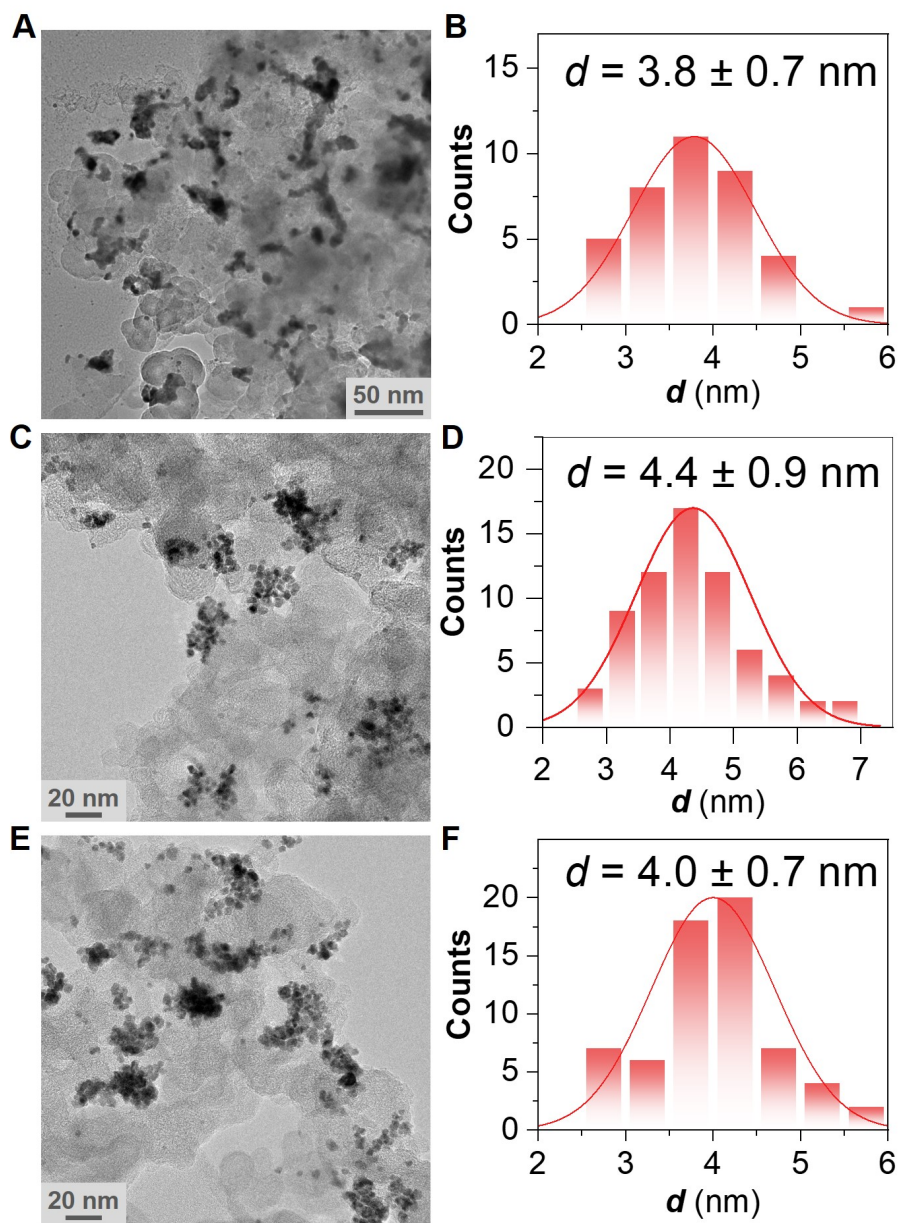
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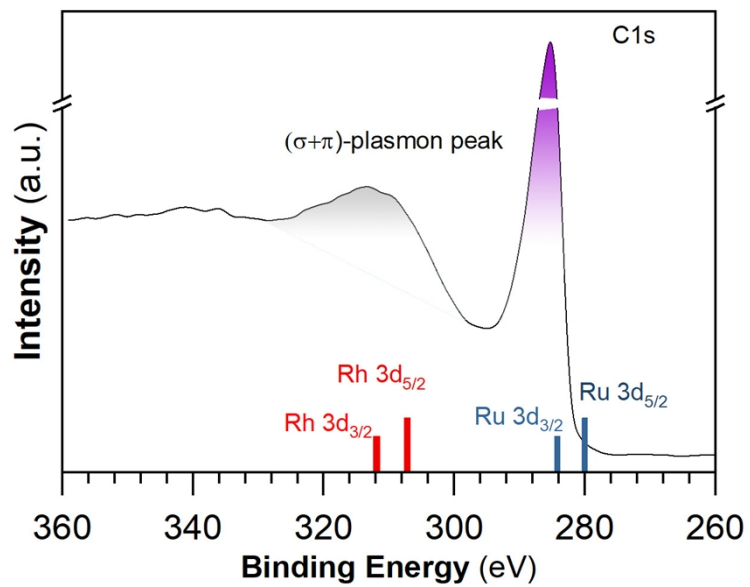
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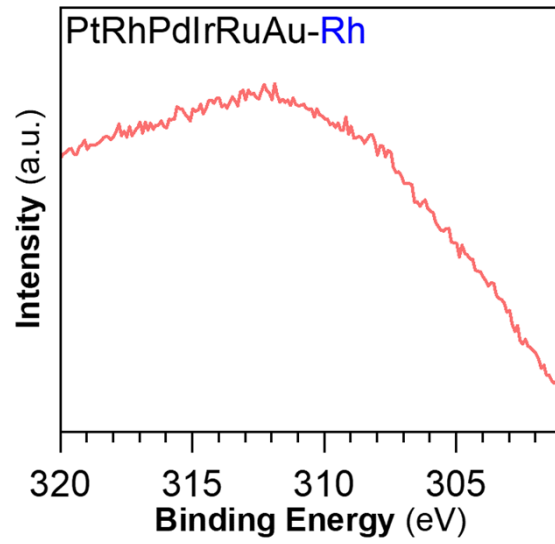
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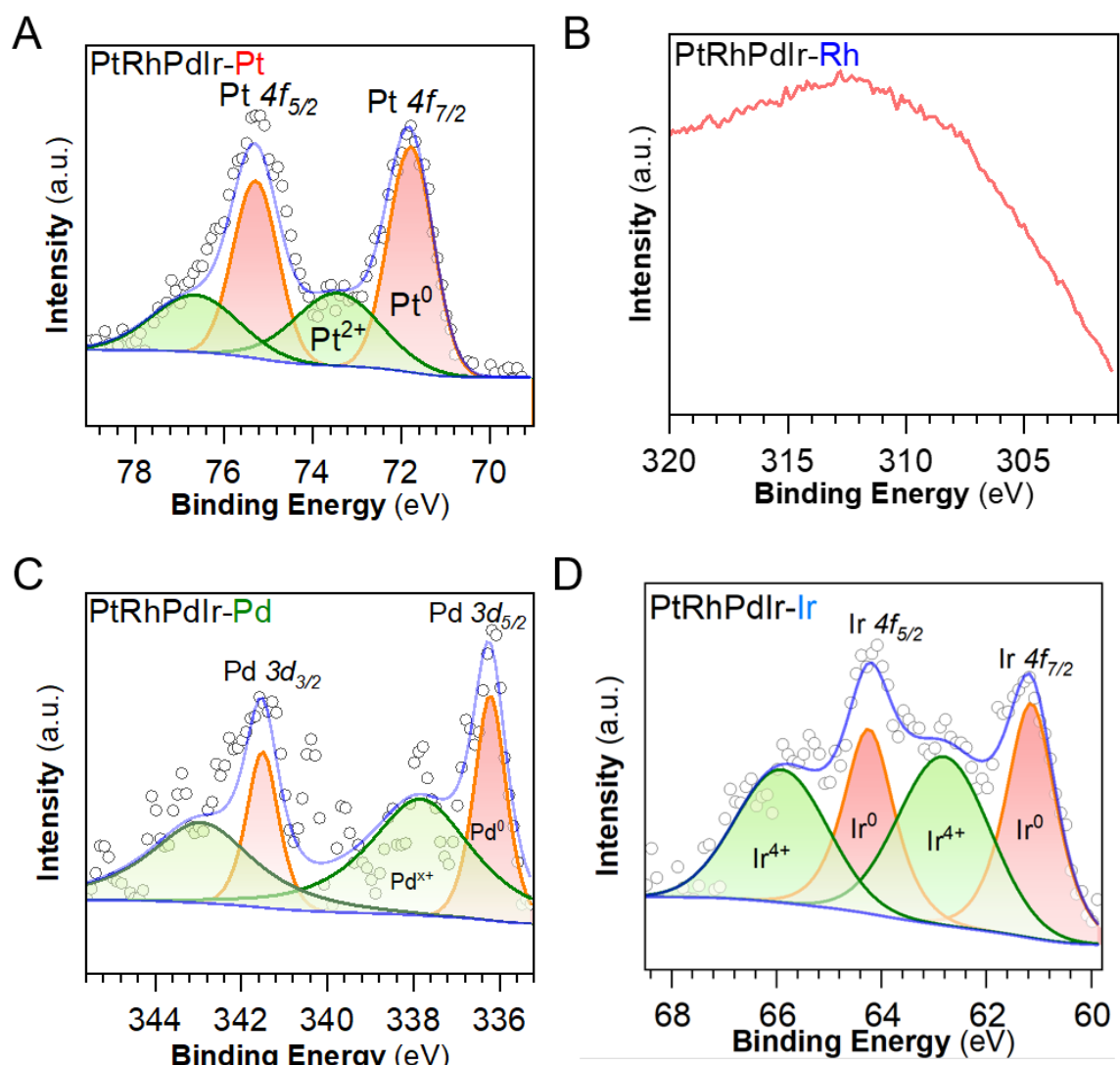
**Figure S1.** TEM images and corresponding histogram of size distribution for (A and B) PtRhPdIr, (C and D) PtRhPdIrRu and (E and F) PtRhPdIrAu NPs.



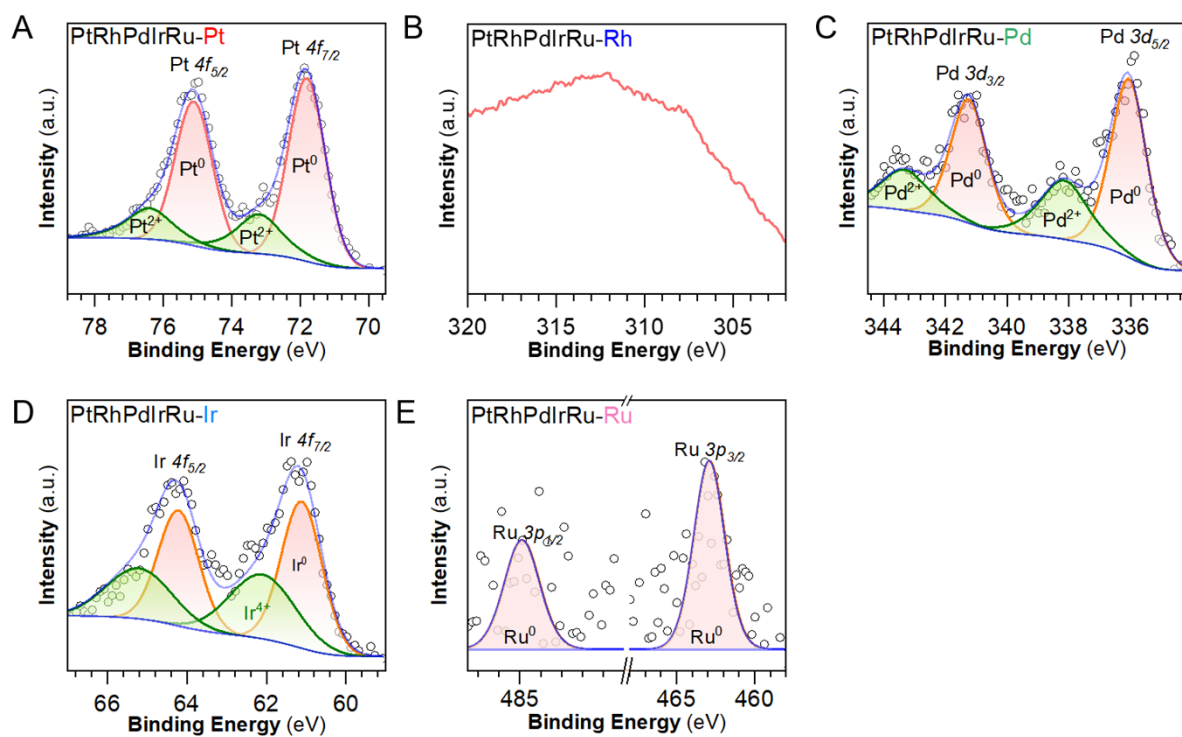
**Figure S2** XPS spectrum from 260 to 360 eV for PtRhPdIrRuAu HEA NPs.



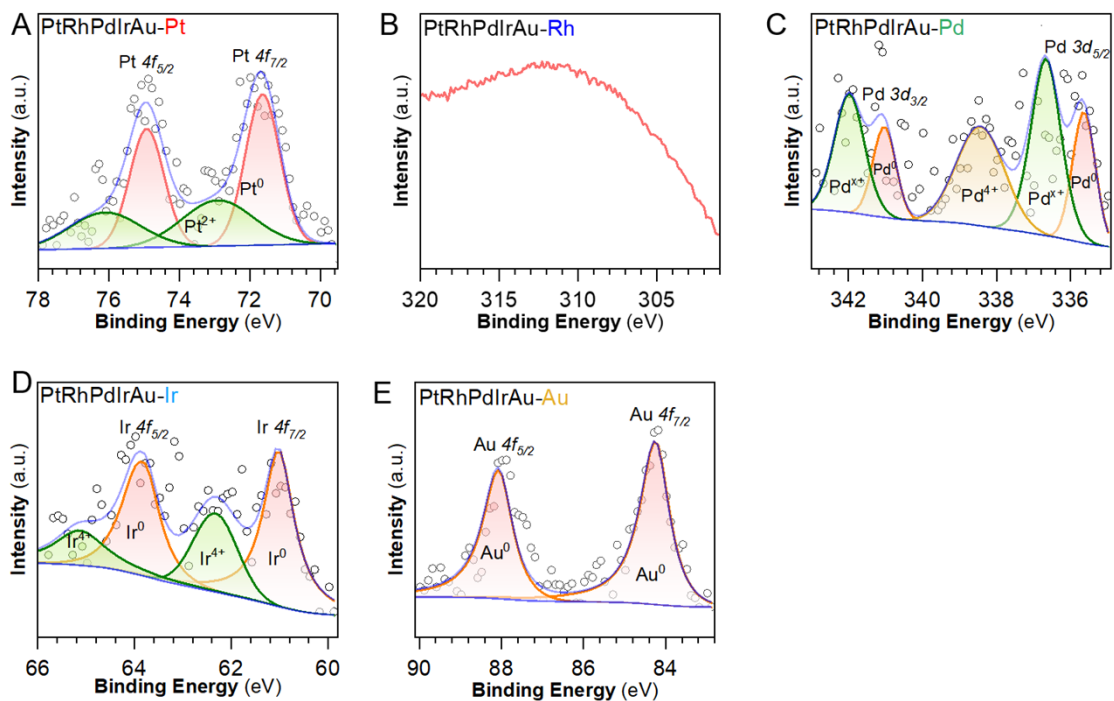
**Figure S3** XPS spectrum from 301 to 320 eV (Rh 3d) for PtRhPdIrRuAu HEA NPs.



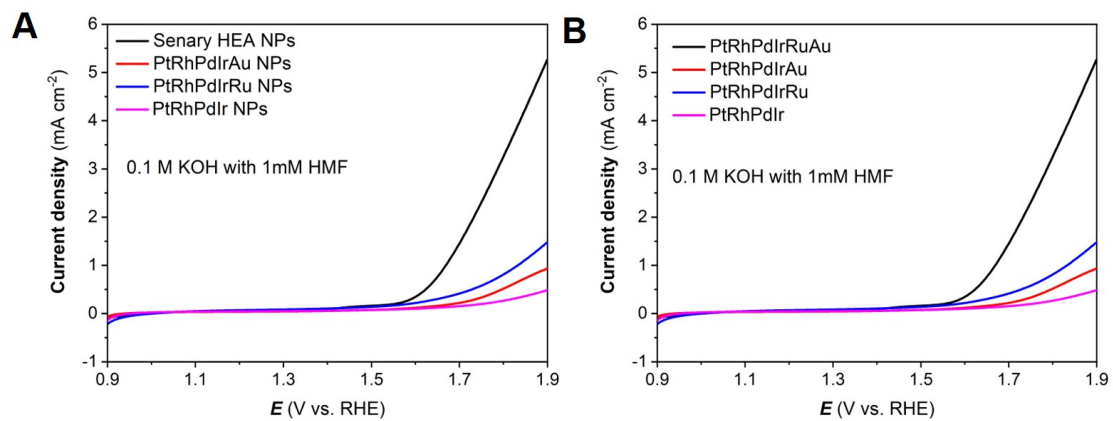
**Figure S4** XPS spectra of (A) Pt 4f, (B)Rh 3d, (C)Pd 3d, and (D) Ir 4f for PtRhPdIr HEA NPs.



**Figure S5.** XPS spectra of (A) Pt 4f, (B) Rh 3d, (C) Pd 3d, (D) Ir 4f, and (E) Ru 3p for PtRhPdIrRu HEA NPs.

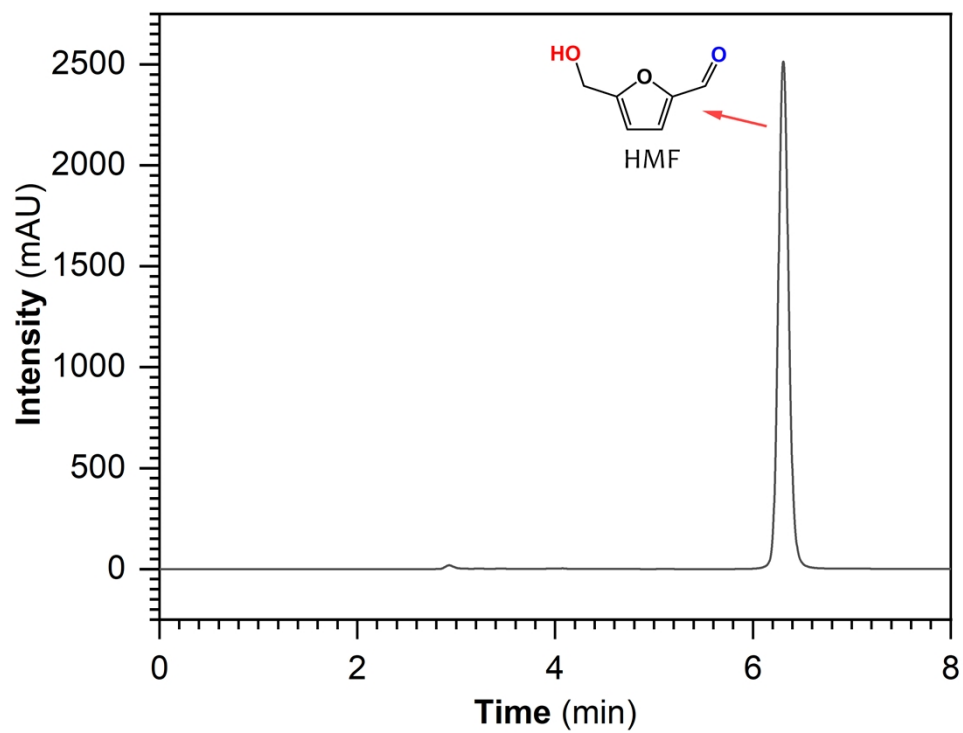


**Figure S6.** XPS spectra of (A) Pt 4f, (B) Rh 3d, (C) Pd 3d, (D) Ir 4f, and (E) Au 4f for PtRhPdIrAu HEA NPs.

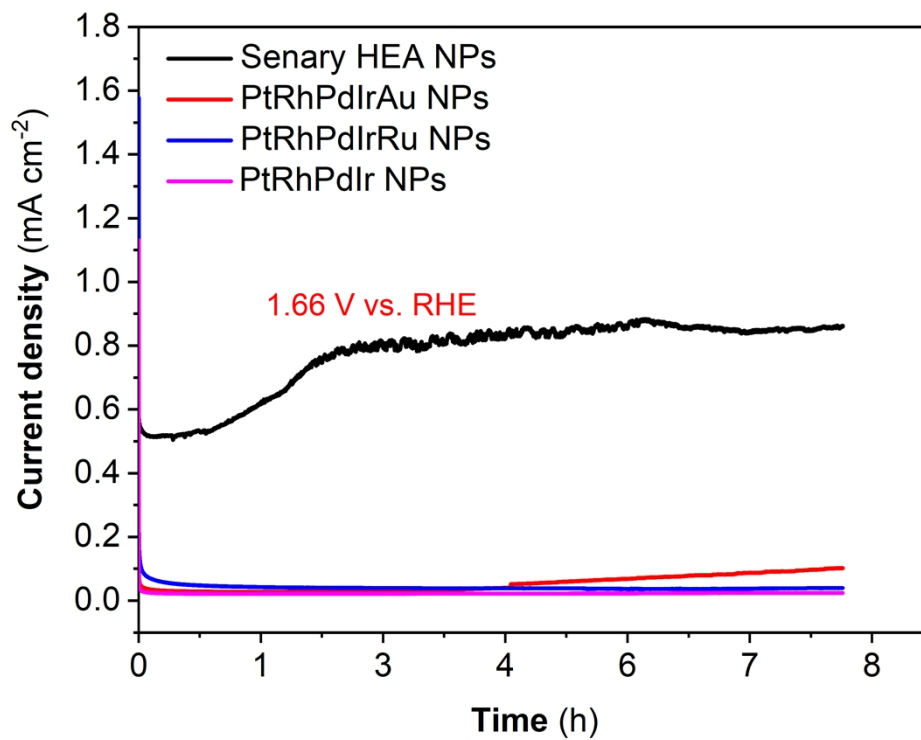


**Figure S7.** Comparison of LSV curves of HEA NPs in 0.1 M KOH without/with 1 mM HMF at a scan rate of 10 mV s<sup>-1</sup>.

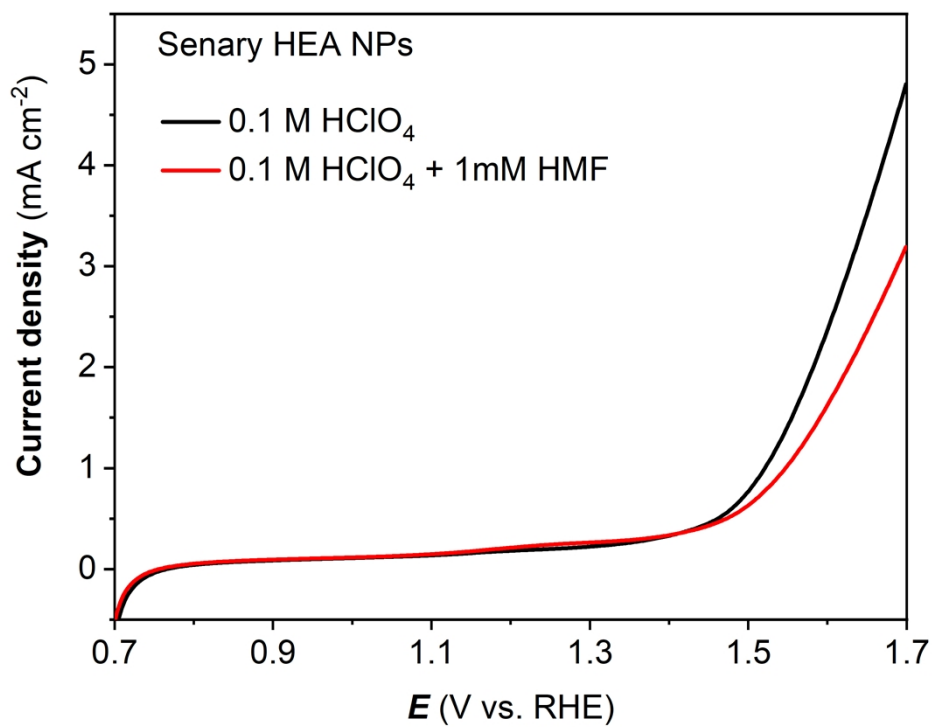




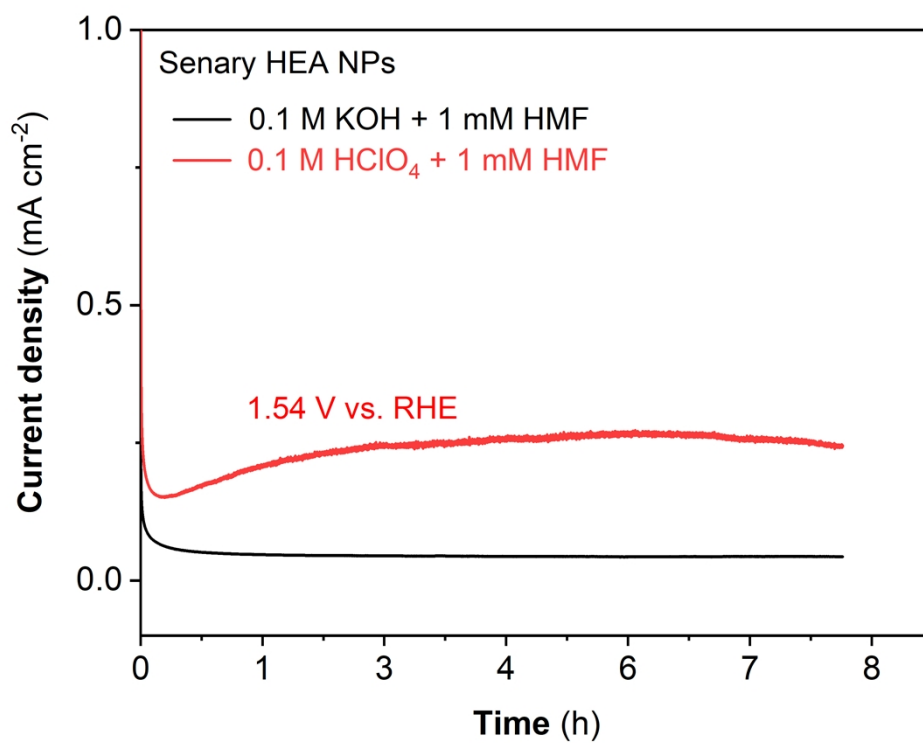
**Figure S8.** HPLC chromatogram of 0.1 M KOH + 1 mM HMF.



**Figure S9.** Chronoamperometric curves of HEA NPs in 0.1 M KOH + 1 mM HMF at 1.66 V vs. RHE.



**Figure S10.** Comparison of LSV curves of Senary HEA NPs in 0.1 M HClO<sub>4</sub> without/with 1 mM HMF at a scan rate of 10 mV s<sup>-1</sup>.



**Figure S11.** Chronoamperometric curves of Senary HEA NPs in alkaline/acidic electrolytes at 1.54 V vs. RHE.

**Table S1.** Selectivity of HMF oxidation products over HEA NPs in alkaline/acidic electrolytes with 1 mM HMF at different potential for 8 h.

Catalyst	E(V vs RHE)	Electrolyte	Conversion (%)	Selectivity (%)			
				FDCA	HMFCFA	FFCA	DFC
PtRhPdIr	1.66	0.1 M KOH	8.12	0	39.3	16.0	44.6
PtRhPdIrAu	1.66	0.1 M KOH	9.68	20.9	4.2	25.9	48.8
PtRhPdIrRu	1.66	0.1 M KOH	17.04	24.2	7.5	27.7	40.4
PtRhPdIrRuAu	1.66	0.1 M KOH	48.41	18.0	63.4	0.5	17.9
PtRhPdIrRuAu	1.54	0.1 M KOH	21.61	11.5	16.3	29.4	42.5
PtRhPdIrRuAu	1.54	0.1M HClO <sub>4</sub>	34.92	0	8.4	17.2	74.2

**Table S2.** The selectivity in different products on reported noble metal based catalysts for the electrochemical oxidation of HMF.

Catalysts	Electrolyte/HMF concentration	Reaction time [h]	$E$ (V vs RHE)	selectivity [%]			Ref
				DFE	HMFCFA	FDCA	
Pd/C	0.02 M	1	0.6	<1	25	11	1
Pd <sub>2</sub> Au <sub>1</sub> /C	0.02M	1	0.6	<1	30	8	
Pd <sub>1</sub> Au <sub>2</sub> /C	0.02M	1	0.6	—	59	25	
Au/C	0.02M	1	0.6	—	98	1	
Pd/C	0.02M	1	0.9	—	70	29	
Pd <sub>2</sub> Au <sub>1</sub> /C	0.02M	1	0.9	—	35	64	
Pd <sub>1</sub> Au <sub>2</sub> /C	0.02M	1	0.9	—	16	83	
Au/C	0.02M	1	0.9	—	98	1	
Pd/C	0.02M	1	1.2	—	71	3	
Pd <sub>2</sub> Au <sub>1</sub> /C	0.02M	1	1.2	—	61	22	
Pd <sub>1</sub> Au <sub>2</sub> /C	0.02M	1	1.2	—	60	36	
Au/C	0.02M	1	1.2	—	81	14	
Pd <sub>14</sub>	0.005M	2	0.82	—	—	12	2
Au <sub>14</sub>	0.005M	2	0.82	—	—	7.7	
Au <sub>7</sub> /Pd <sub>7</sub>	0.005M	2	0.82	—	—	20.6	
Pd <sub>7</sub> /Au <sub>7</sub>	0.005M	2	0.82	—	—	23.8	
(AuPd) <sub>7</sub>	0.005M	2	0.82	—	—	22.5	
Ru <sub>1</sub> /NiO	1.0M KOH	10C	1.3	9	73	1	3
Ru <sub>1</sub> /NiO	1.0M KOH	10C	1.5	14	40	29	
Ru <sub>1</sub> /NiO	1.0M KOH	10C	1.7	10	41	30	
Pt	0.02M	25C	2	10.5	0	0	4
Pt	0.02M	50C	2	24.8	0	0	
Pt	0.02M	100C	2	14.8	0	0	
Pt	0.02M	150C	2	16.3	0	0	
Pt	0.02M	200C	2	9.6	0	0	
Pt	0.02M	250C	2	5.3	0	<1	
Pt/C	0.1M	17h	—	72	2	2	5
PtRu(1:1)/C	0.1M	17h	—	89	0	0	
Ru/C	0.1M	17h	—	32	20	14	
Pt/Fe <sub>3</sub> O <sub>4</sub> /rGO	0.1M KOH	20h	0.85	—	35.8	—	6
Pt/Fe <sub>3</sub> O <sub>4</sub> /rGO	0.1M K <sub>2</sub> SO <sub>4</sub>	20h	0.85	94.4	—	—	

## References

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