Supplementary Information

for

In-situ Capturing Site-to-Site Reactive Species in CO_2-Laser Patterned High-Entropy Alloy Nanoflowers for Robust Alkaline Seawater Electrolysis

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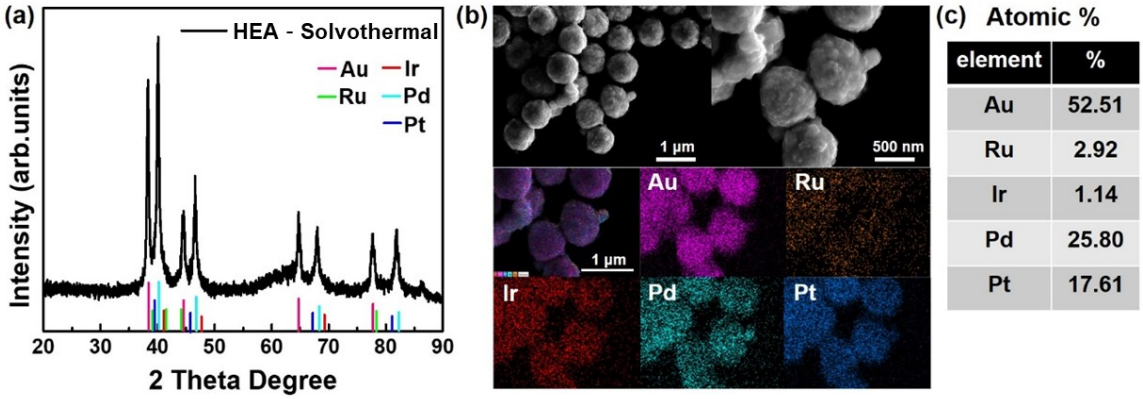
Materials

Hydrogen gold (III) chloride ($HAuCl_4 \cdot 3H_2O$, 99.9%), Ruthenium (III) chloride hydrate ($RuCl_3 \cdot xH_2O$, 98%), hydrogen gold (III) chloride ($HAuCl_4 \cdot 3H_2O$, 99.9%), potassium palladium (II) chloride (K_2PdCl_4, 98%), and potassium platinum (II) chloride (K_2PtCl_4, 98%) were supplied by Sigma-Aldrich, USA. Iridium (III) chloride hydrate ($IrCl_3 \cdot xH_2O$, 99.9%) was obtained from STREM chemicals, USA. Hydrochloric acid (HCl, 35%), ethanol (high-performance liquid chromatography grade, 99.5%), and potassium hydroxide (KOH, extra pure flakes, 93%) were purchased from Daejung Chemicals, South Korea. All chemicals were used as-received without further purification.

Characterization techniques

Surface morphology and elemental compositional properties of the synthesized HEAs were assessed via high-resolution transmission electron microscopy (HR-TEM) using a FEI Talos F200X TEM (Thermo Fisher Scientific, USA) instrument under an operating voltage of 200 kV. The elemental mapping images were recorded using a Spectra Ultra-X EDX detector attached with HRTEM (Thermo Fisher Scientific, USA) under an operating voltage of 80 kV. Field-emission scanning electron microscope (FESEM Apreo S, Thermo Fisher) is used record surface structures. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance A25 diffractometer (Germany) with Cu-Kα radiation (λ = 0.1541 nm) at a scan rate of 5°/min. UV-visible absorption spectra were collected from a UV-visible spectroscopy (GENESYS 10S, Thermo Fisher Scientific). The quantitative analysis of the elemental composition of the materials was performed in an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer, Optima 8300DV). Raman spectra were recorded in

Raman imaging microscope with a 532 nm continuous laser (DXR2xi, Thermo Scientific). The elemental state and binding energies of the samples were studied using X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa G2).



element	%
Au	52.51
Ru	2.92
Ir	1.14
Pd	25.80
Pt	17.61

Fig. S1 (a) XRD, (b) FE-SEM images with elemental mapping, and (c) ICP-OES of HEA synthesized via solvothermal process.

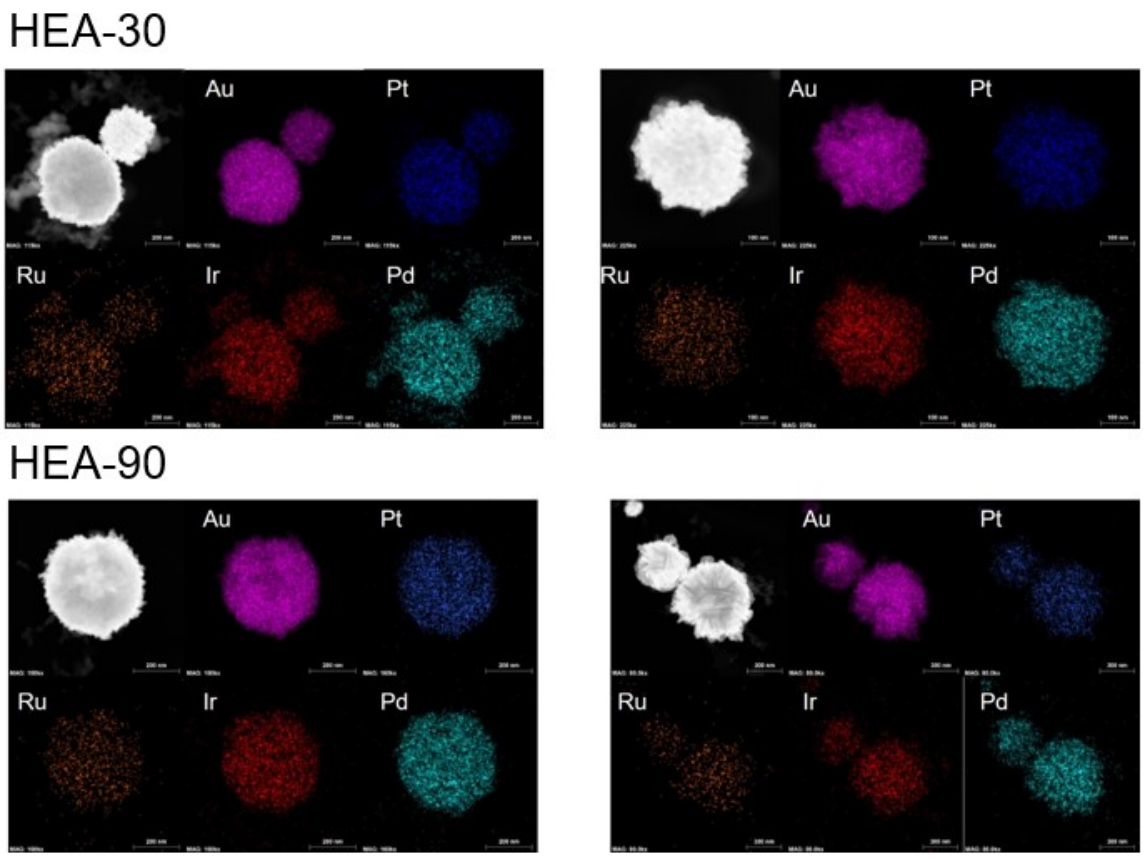


Fig. S2 HAADF-STEM element mapping images of non-flowers (left) and flower (right) in HEA-30 and HEA-90 synthesized by CW CO_2 laser irradiation.

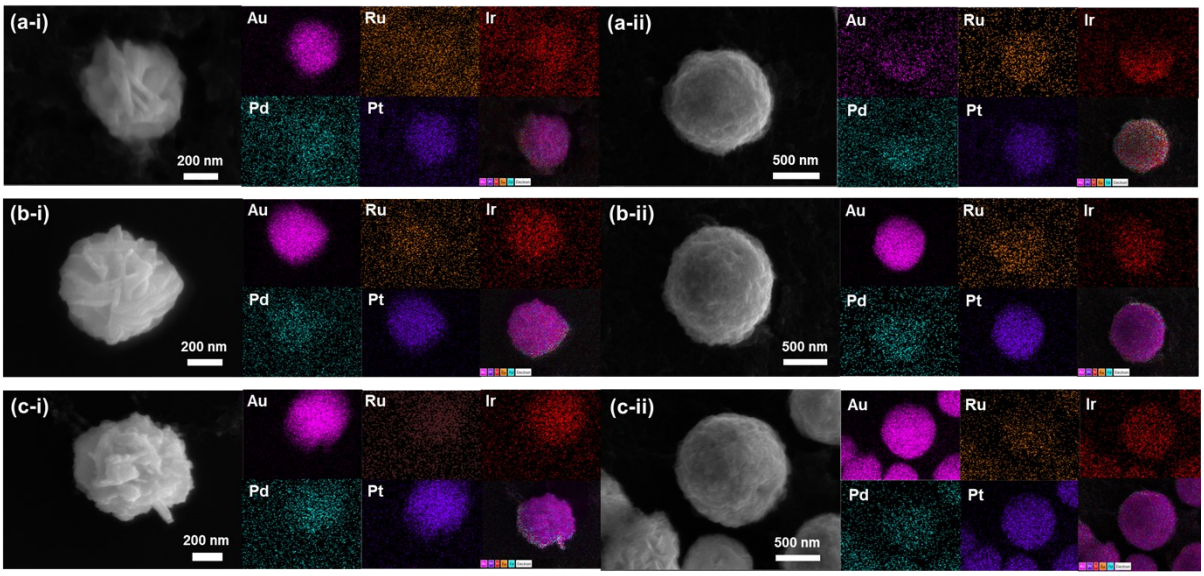


Fig. S3 FE-SEM EDS elemental mapping images of flowers: (a-i) HEA-30, (b-i) HEA-60 and (c-i) HEA-90. FE-SEM EDS elemental mapping images of non-flowers: (a-ii) HEA-30, (b-ii) HEA-60 and (c-ii) HEA-90.

Table S1. ICP-OES results of HEA by CW CO_2 laser.

Atomic%

	Pt	Ir	Au	Ru	Pd
HEA-30	5.51	16.62	33.36	22.31	22.19
HEA-60	4.68	16.85	34.01	30.84	13.63
HEA-90	6.87	15.19	34.26	33.41	10.27

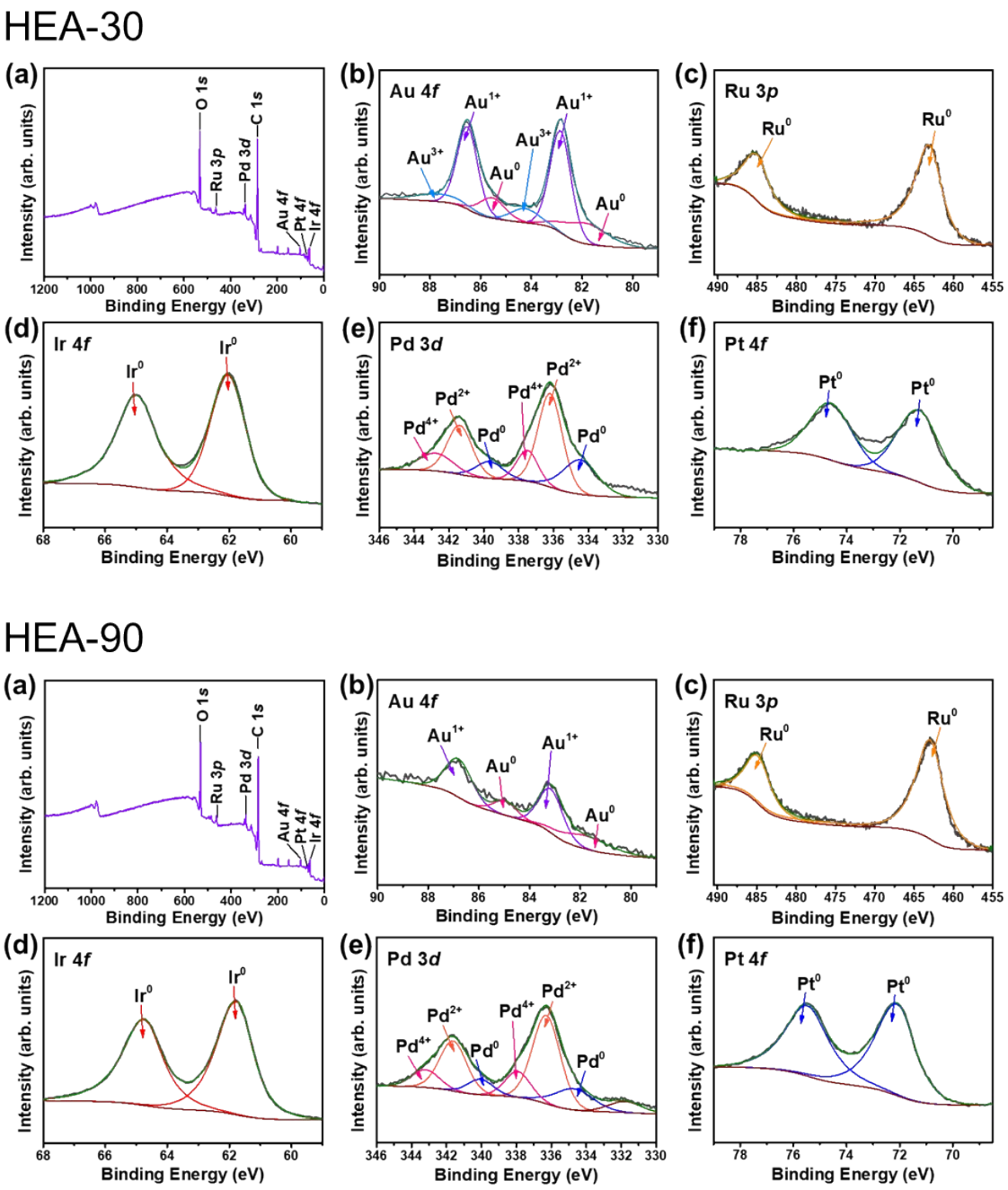


Fig. S4 XPS spectra of HEA-30 and HEA-90; (a) XPS survey, (b) core-spectra Au 4*f*, (c) Ru 3*p*, (d) Ir 4*f*, (e) Pd 4*f*, and (f) Pt 4*f*

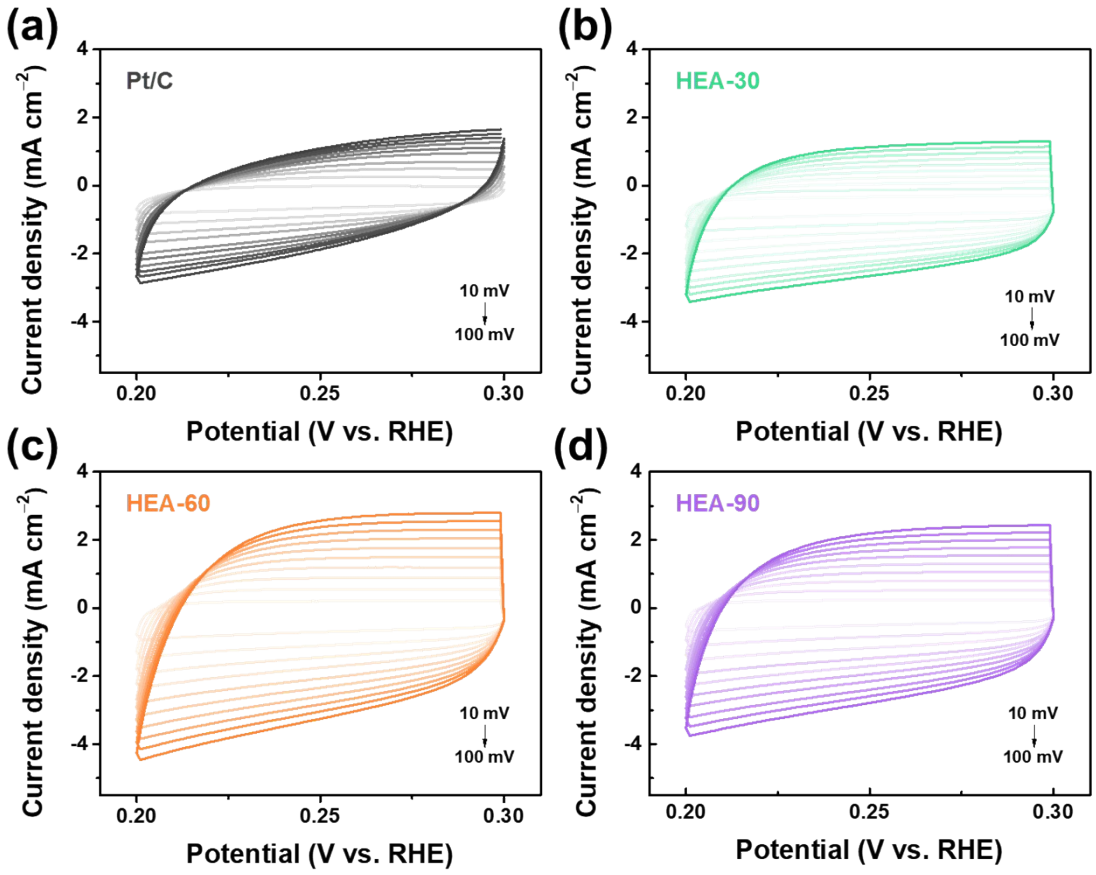


Fig. S5 The calculated active site and CV curves at different scan rates of 10 to 100 mV s^{-1} in 1.0 M KOH for HER. (a) Pt/C, (b) HEA-30, (c) HEA-60, and (d) HEA-90.

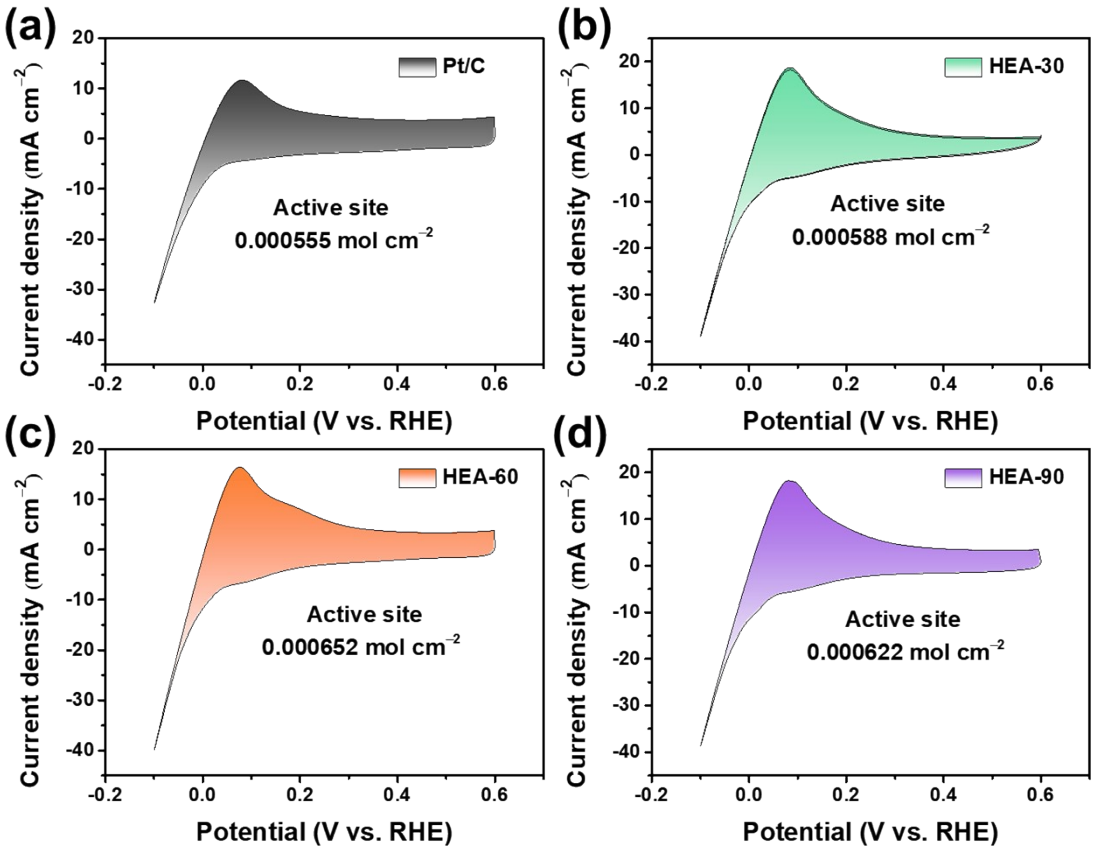


Fig. S6 The CV profiles for the synthesized HEAs and commercial Pt/C, HEA-30, HEA-60, and HEA-90 samples attained in the potential range of -0.1 to 0.6 V vs. RHE in 1.0 M KOH at 50 mV/s.

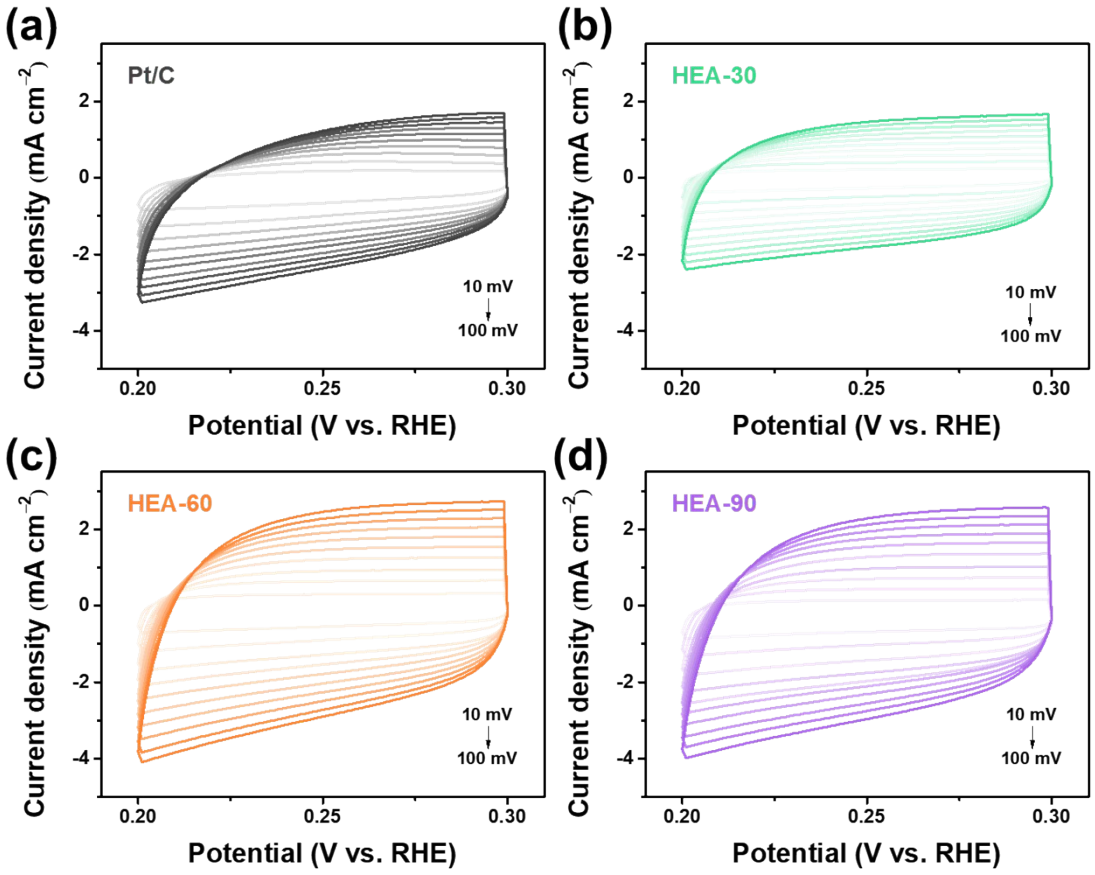


Fig. S7 The CV curves at different scan rates of 10 to 100 mV s^{-1} in 1.0 M KOH+0.5 M NaCl for HER; (a) Pt/C, (b) HEA-30, (c) HEA-60, and (d) HEA-90.

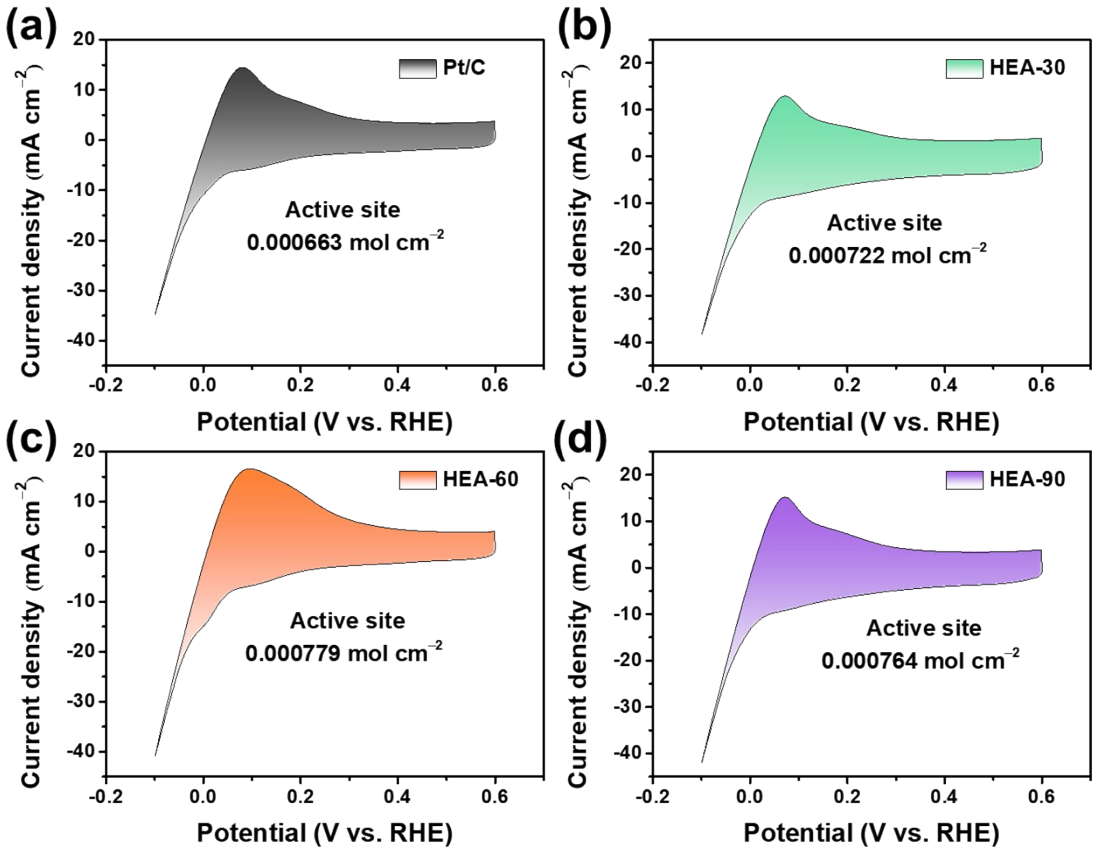


Fig. S8 The calculated active sites using the CV profiles for the synthesized HEAs and commercial Pt/C, HEA-30, HEA-60, and HEA-90 samples in 1.0 M KOH + 0.5 M NaCl solution at 50 mV/s.

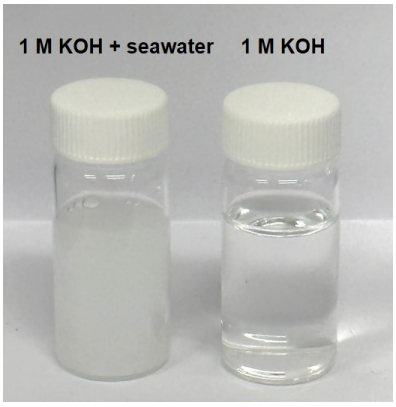


Fig. S9 Seawater was collected from Namildae beach in Suncheon, South Korea.

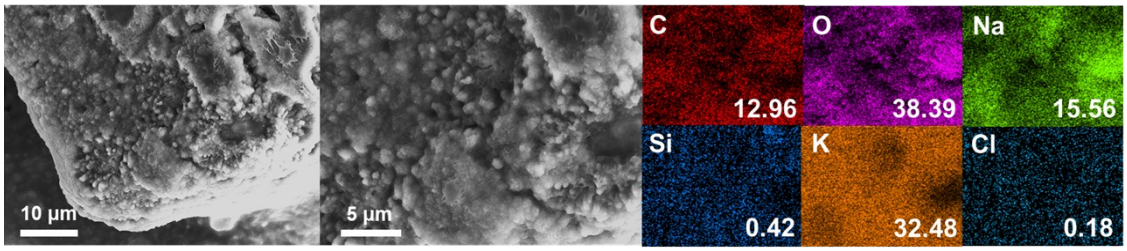


Fig. S10 FE-SEM and EDS mapping of the HEA-60 electrode after HER test in alkaline seawater reveal the presence of Na, K, Cl, and Si from natural seawater, which cover the electrode surface and block the active sites.

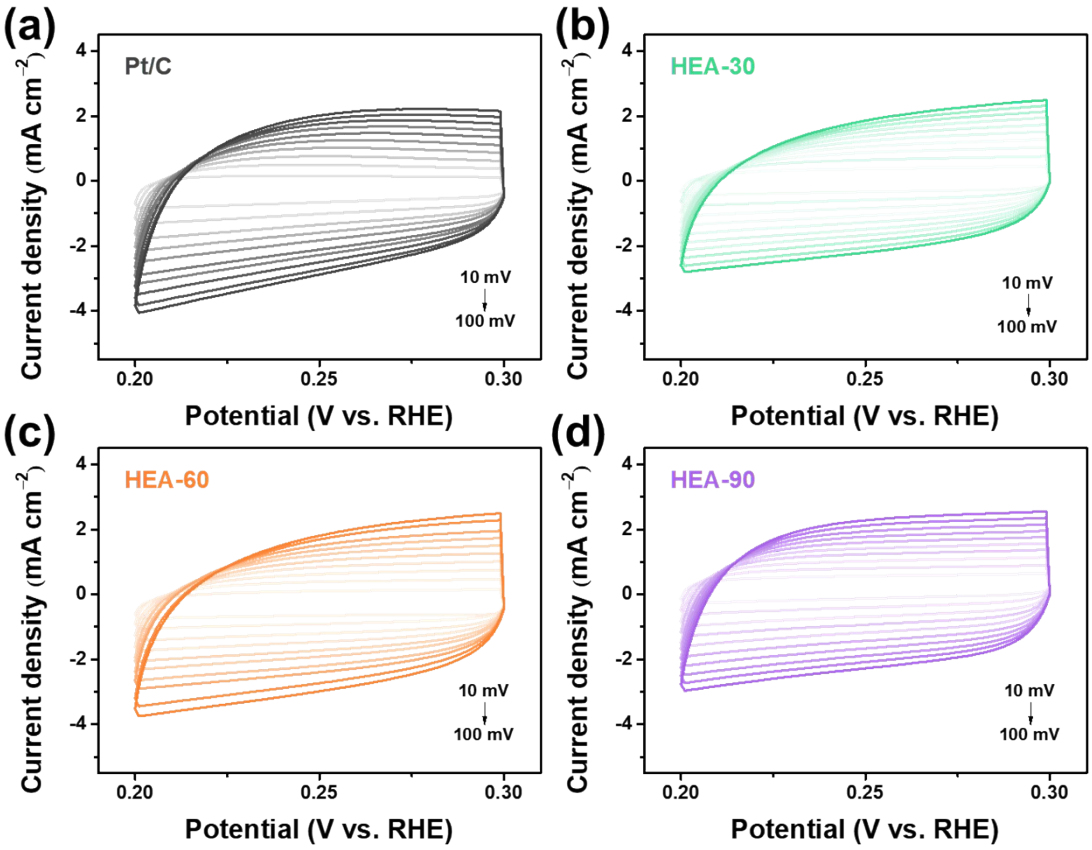


Fig. S11 The CV curves at different scan rates of 10 to 100 mV s^{-1} in 1.0 M KOH + natural seawater for HER; (a) Pt/C, (b) HEA-30, (c) HEA-60, and (d) HEA-90.

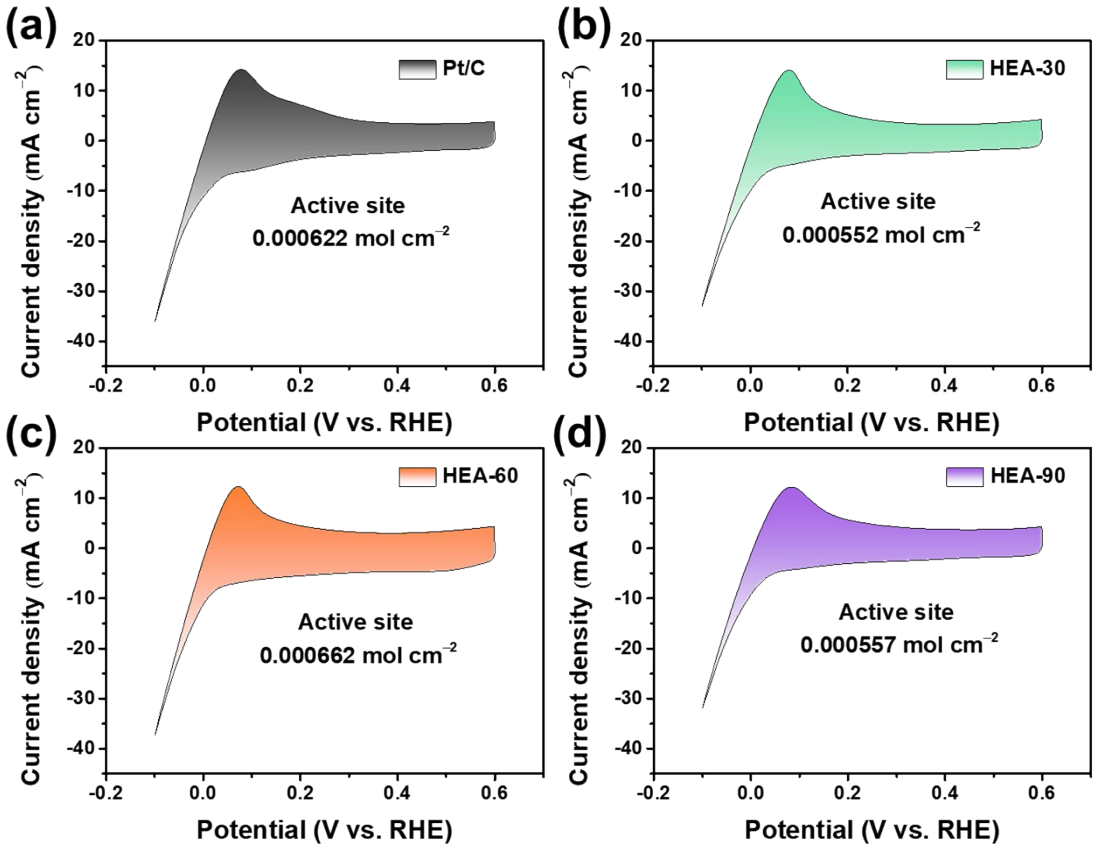


Fig. S12 The calculated active sites using the CV profiles for the synthesized HEAs and commercial Pt/C, HEA-30, HEA-60, and HEA-90 samples in 1.0 M KOH in natural seawater solution at 50 mV/s.

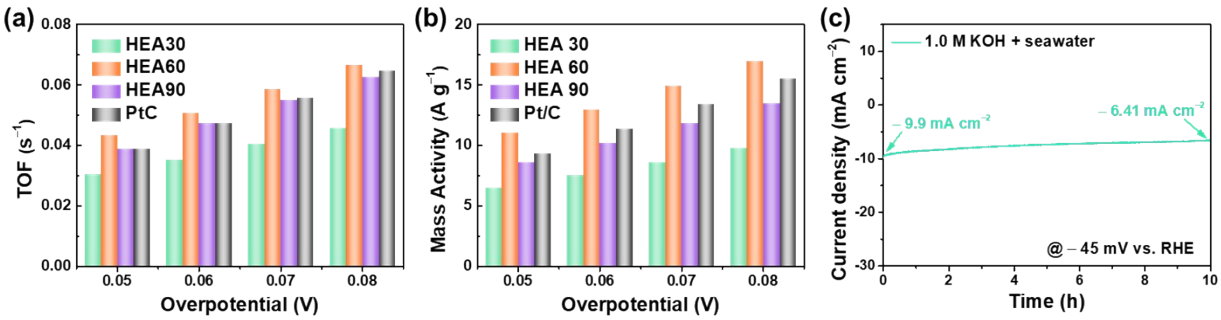


Fig. 13 The HER performance of Pt/C, HEA-30, HEA-60, and HEA-90 in 1.0 M KOH in natural seawater; (a) TOF, (b) Mass activity, and (c) long-term stability.

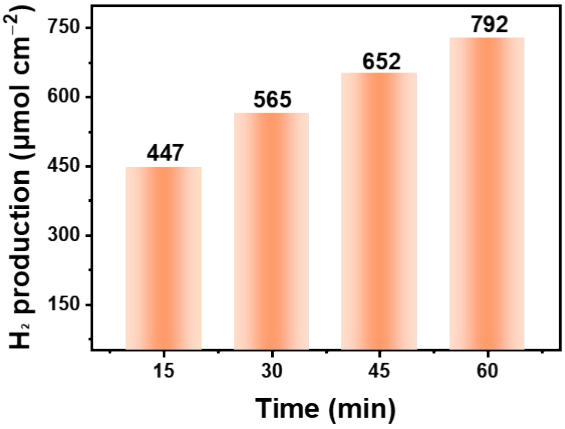


Fig. S14 The measured amount of H_2 varies with reaction time for the fabricated IrO2(+)||HEA-60(−) alkaline seawater electrolyzer.

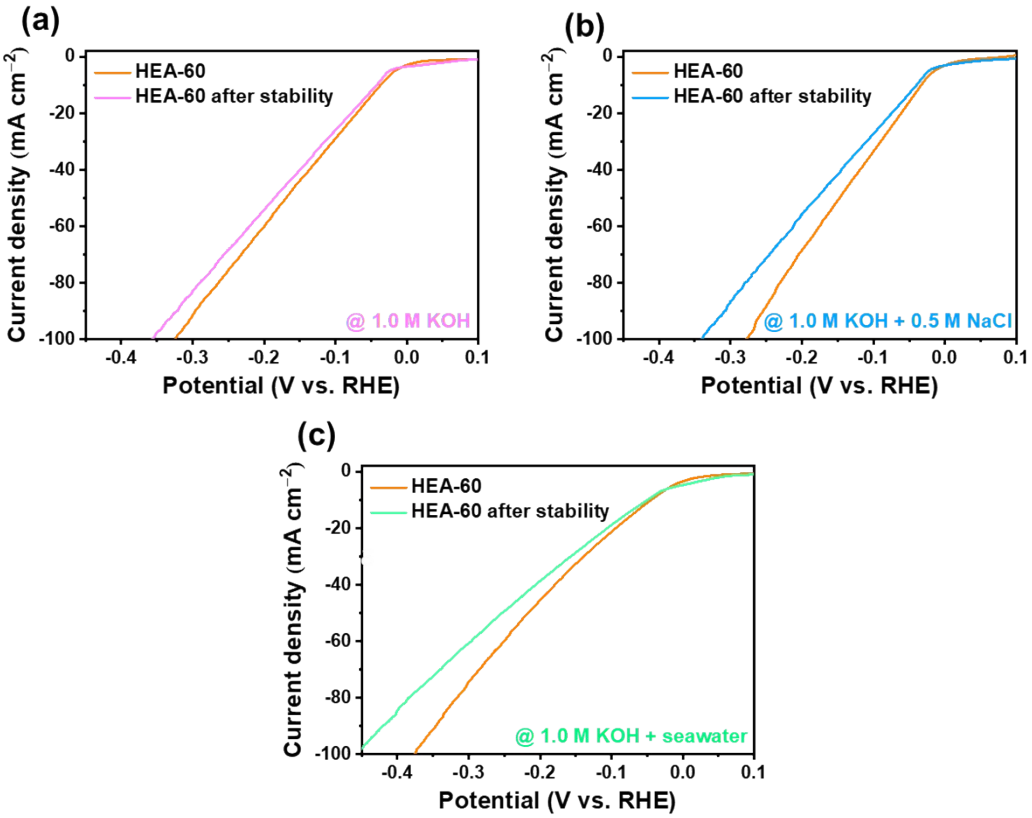


Fig. S15 The LSV polarization curves of the before and after HER stability test in various electrolytes: (a) 1.0 M KOH, (b) 1.0 M KOH + 0.5 M NaCl and (c) 1.0 M KOH + Seawater.

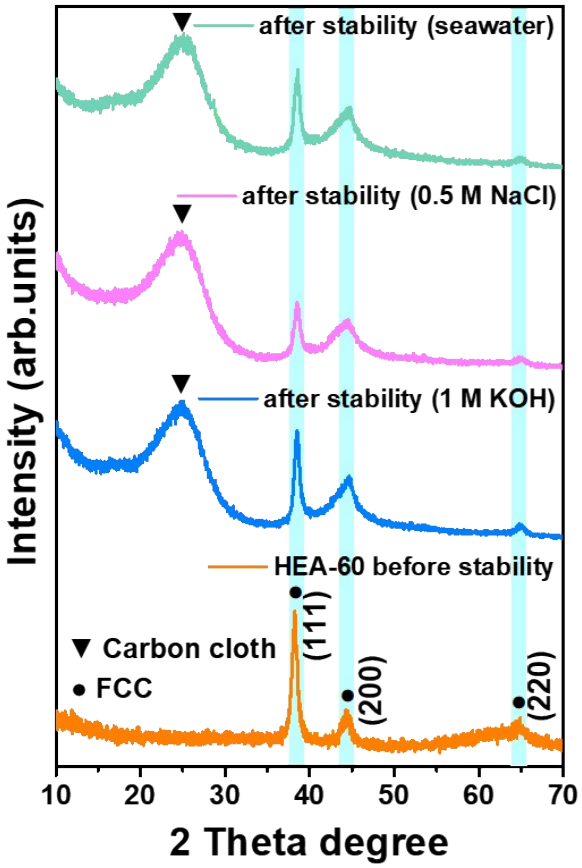


Fig. S16 The XRD patterns of HEA-60 before and after HER stability test in various electrolytes.

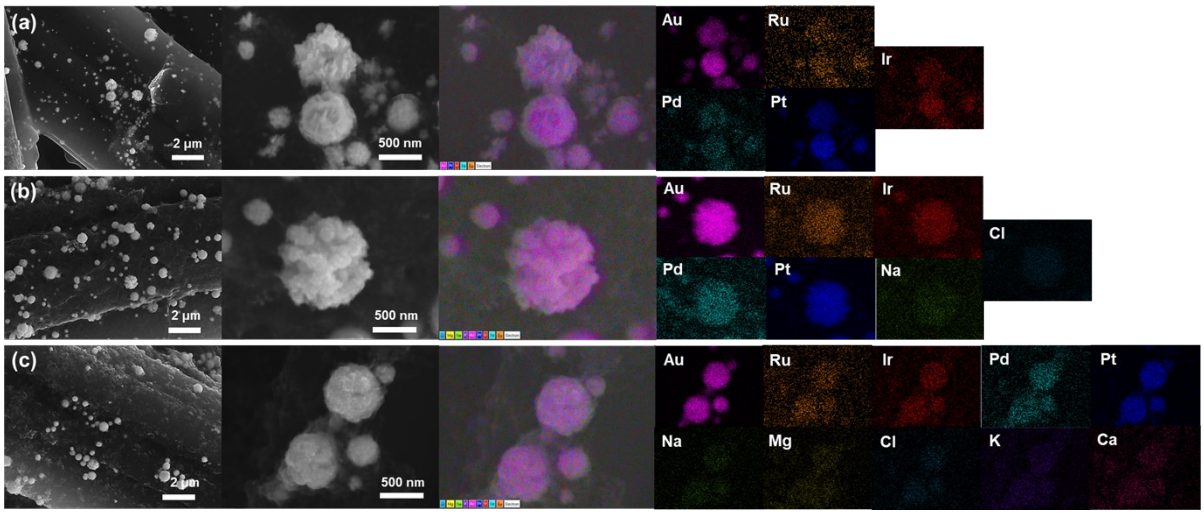


Fig. S17 FE-SEM with EDS mapping images of the HEA-60 catalyst after HER stability test in various electrolytes: (a) 1.0 M KOH, (b) 1.0 M KOH + 0.5 M NaCl, and (c) 1.0 M KOH + Seawater.

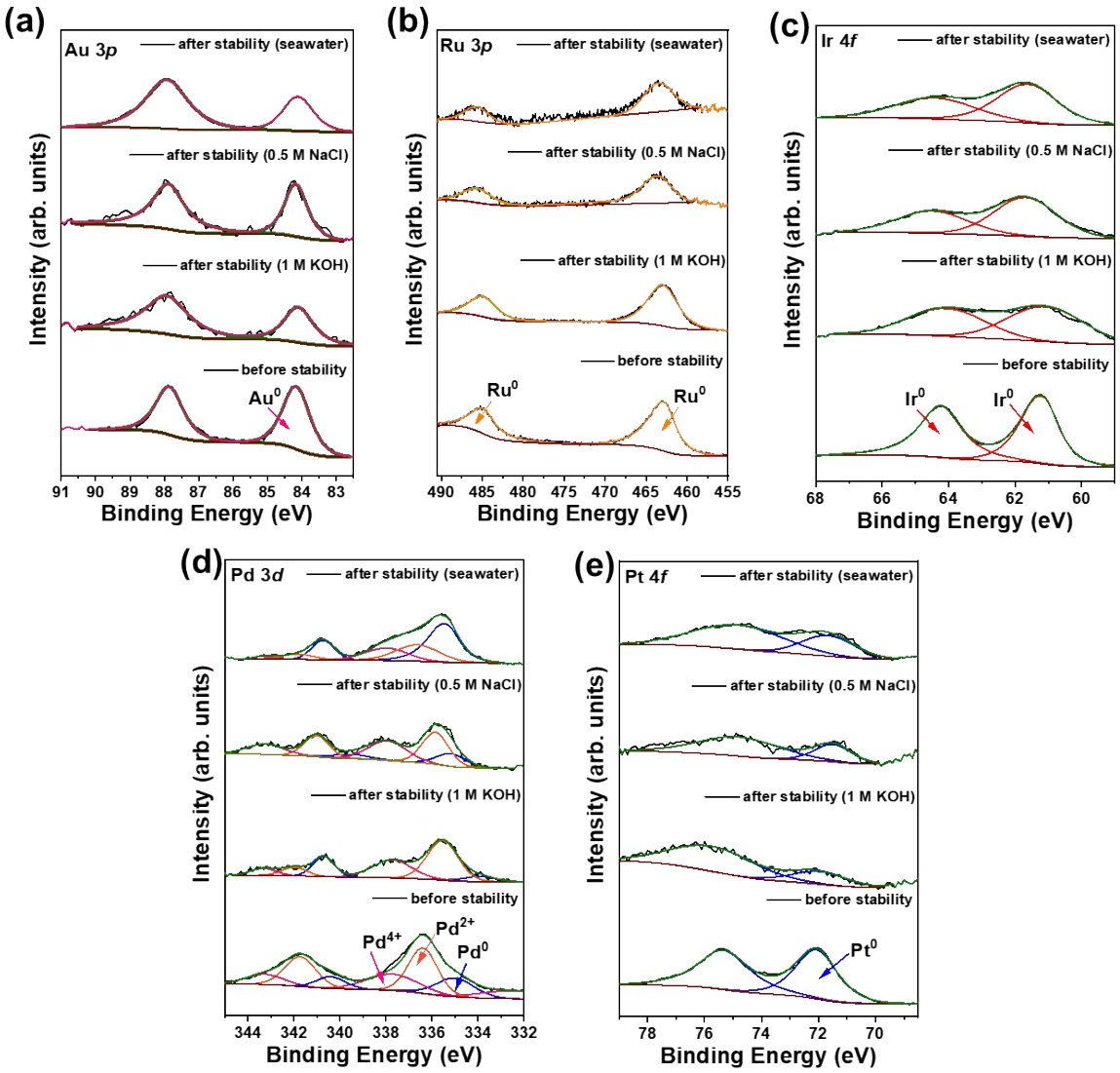


Fig. S18 XPS spectra of the before and after HER stability test in various electrolytes: (a) Au 3*p*, (b) Ru 3*p*, (c) Ir 4*f*, (d) Pd 3*d*, and (e) Pt 4*f*.

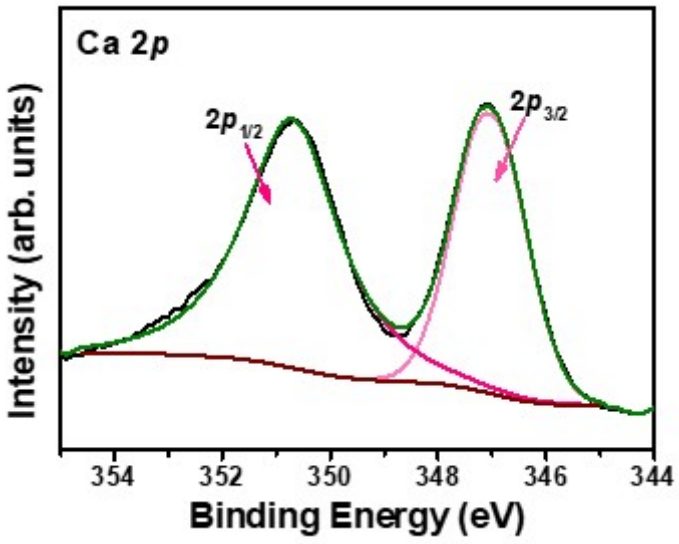


Fig. S19 XPS spectra of the Ca 2*p* after-stability test for alkaline seawater.

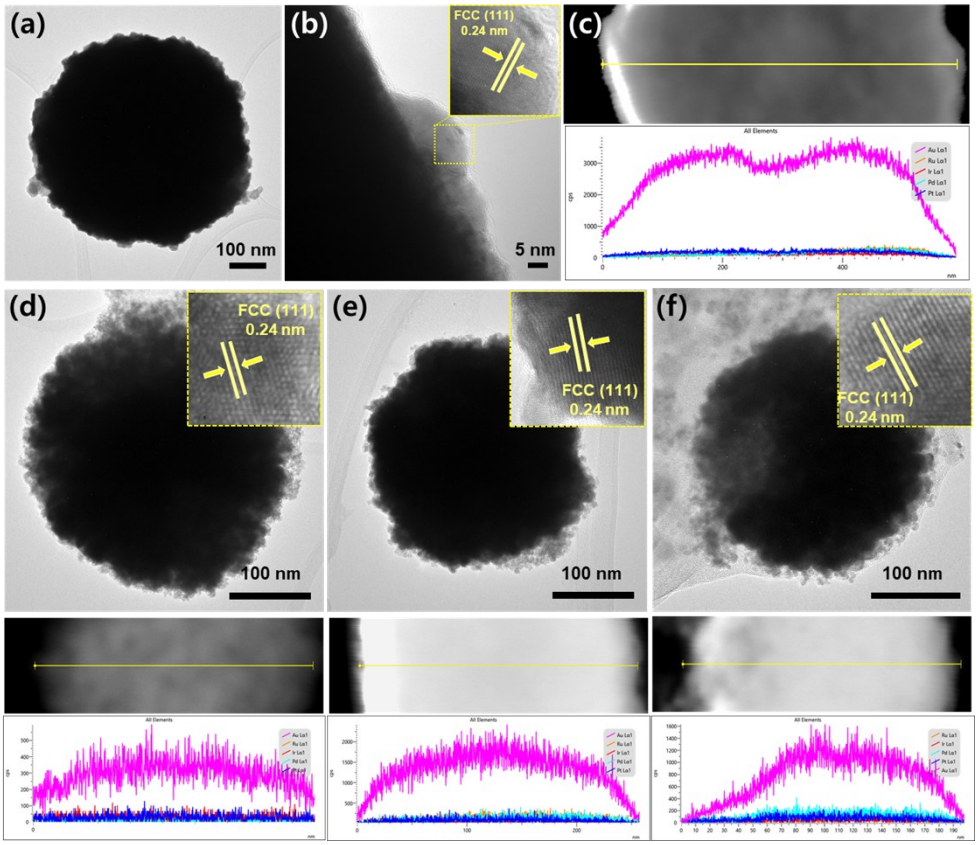


Fig. S20 (a-b) HRTEM images with low and high magnification, and (c) line scan EDS spectrum of HEA-60 before stability test. HRTEM and line scan EDS spectra of HEA-60 after stability test in various electrolyte solutions: (d) 1.0 M KOH, (e) 1.0 M KOH + 0.5 M NaCl, and (e) 1.0 M KOH + seawater.