Electronic Supplementary Information (ESI)

Acanthosphere-like PtRuRhPdAuIr high-entropy alloy as an efficient electrocatalyst for hydrogen evolution in both acidic and alkaline electrolytes

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1. Experimental

1.1 Materials

Potassium chloroplatinate (K_2PtCl_6, AR reagent), ruthenium trichloride ($RuCl_3$, GR reagent), rhodium chloride trihydrate ($RhCl_3.3H_2O$, AR reagent), palladium chloride ($PdCl_2$，AR reagent), tetrachloroauric acid trihydrate ($HAuCl_4.3H_2O$, AR reagent), iridium chloride ($IrCl_3$, AR reagent), urea ($CO(NH_2)_2$, >99%), choline chloride ($HOC_2H_4N(CH_3)_3Cl$, 99%), potassium hydroxide (KOH, AR reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4, AR reagent) was purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. (Shanghai, China).

1.2 Preparation of DES

The choline chloride-urea (ChCl-U) based DES was prepared from a mixture of ChCl and urea in a molar ratio of 1:2.[1-4] The mixture was heated and stirred in a round bottomed flask at 80 °C until forming a homogenous transparent liquid.

1.3 Preparation of PtRuRhPdAuIr HEA

The PtRuRhPdAuIr HEA was prepared by electrochemical cyclic voltammetry (CV) method with scanning potential range between –0.2 and –1.2 V (vs. Pt) at 50 mV s^{-1} at 60 ºC for 30 cycles in ChCl-U based DES solution containing K_2PtCl_6, $RuCl_3$, $RhCl_3$, $PdCl_2$, $HAuCl_3$ and $IrCl_3$ precursors.

The concentration of $HAuCl_3$ is 24.28 mM. The concentration of other elements is 10 mM. The ratio of the amount of each metal substance in the deposited solution is Pt/Ru/Ir/Au/Pd/Rh = 10/5/5/1/1/1. All electrodeposition experiments were carried out in a standard three-electrode cell with a platinum wire counter electrode and a platinum quasi-reference electrode. The working electrode, glassy carbon electrode (GCE, Φ = 6 mm), was polished mechanically by using Al_2O_3 polishing powder with sizes of 1.0 and 0.3 μm, respectively.

1.4 Preparation of control group catalysts

After removing one metal element (except Pt), the original mother liquor was prepared by uniformly mixing the components according to their respective ratios, maintaining consistent relative proportions between Pt and the remaining metallic constituents. The preparation conditions of the quinary alloys were completely consistent with those of PtRuRhPdAuIr.

1.5 Characterization

Scanning electron microscopy (SEM) images of PtRuRhPdAuIr HEA was obtained on a SU8010 electron microscope. Transmission electron microscopy (TEM), elemental mapping and energy dispersive X-ray spectroscopy (EDX) measurements were performed by using a FEI Tecnai-F20 electron microscope at an operating voltage of 200 kV. The surface electronic structure of PtRuRhPdAuIr HEA was analyzed by using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi spectrometer (Thermo Scientific, USA). All measured values of the electron binding energy were calibrated with respect to the principal peak of C 1s at 284.5 eV as the internal standard. The Pt, Ru, Rh, Pd, Au and Ir content of samples were quantified by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo ICAP-QC).

1.6 Electrochemical surface area

The electrochemically active surface area (ECSA) of the synthesized PtRuRhPdAuIr HEA and the control group catalysts were measured by CO stripping method.[5,6] Three CV scans over a range of 0.1–1.5 V (*vs.* RHE) at 50 mV s^{-1} in N_2-saturated 0.5 M H_2SO_4 solution were carried out to clean the working electrode and obtain a background CV curve. Inject N_2 into the solution for 0.5 h, the purpose of this operation is to drive away the O_2 dissolved in the solution. At a voltage of 0–0.2 V (vs. RHE), CO is passed in until the hydrogen region basically disappears. Then N_2 is blowing-in the solution, the purpose of this operation is to remove the CO dissolved in the solution. Then the cyclic CV scan is carried out in the voltage range of 0–1.2 V (vs. RHE), and the data of the first circle and the second circle are taken for plotting. The electrochemical active area can be obtained by integrating the peak area. The ECSA of the catalysts was determined under the assumption of 420 μC cm^{-2} of CO adsorbed, which can be calibrated as Eq. (S-1), ECSA = Q_{CO}(mC) / 484(mC·cm^{-2}).

1.7 Electrocatalytic hydrogen evolution reaction testing (0.5 M H_2SO_4)

The HER tests were conducted in an H-type electrolytic cell connected to an electrochemical workstation (CHI 760E, Shanghai Chenhua) in 0.5 M H_2SO_4 solution at ambient conditions. The cathodic and anodic chambers of the reactor were separated by Nafion117 that was boiled successively in 5 % H_2O_2, 0.5 M H_2SO_4, and ultrapure water at 80 °C for 1 h. The reference electrode is a saturated calomel electrode, and the counter electrode is a carbon rod electrode. Firstly, perform 30 cycles of CV scanning at potentials ranging from 0 V to –0.5 V (vs. RHE), using scanning speeds of 100 mV s^{-1} and 50 mV s^{-1}, respectively, in order to activate the electrode and clean the electrode surface to obtain accurate linear sweep voltammetry (LSV) curves. For LSV tests, the scanning range is of 0 V ~ –0.5 V (vs RHE) and the scanning speed is 5 mV s^{-1}. The entire experimental process needs to be conducted in an oxygen free environment, high-purity N_2 needs to be introduced into the reactor for 0.5 h before the experiment begins, and throughout the entire experimental process. The solution internal resistance needs to be obtained at an open circuit voltage of 0 V for ohmic potential drop (*iR*) compensation. Electrochemical impedance spectroscopy (EIS) measurements were tested from 10^5 to 10^{-1} Hz in 0.5 M H_2SO_4 using 10 mV amplitude. For impedance diagrams, there are two important parameters to pay attention. One is Charge Transfer Resistance (*R*ct), which represents the difficulty of ion transfer throughout the entire device, resulting in better catalytic performance. The other is Solution resistance (*R*s), which represents the internal resistance of the solution. In electrochemical testing, this parameter is used for *iR* compensation. In addition, since saturated calomel electrode is used reference electrode, conversion between electrodes is required. The specific calculation formula (S-2) is as follows:

$$E_{(RHE)} = E_{(SCE)} + 0.2438 + 0.059 * pH - 0.9 * iR \qquad \text{(S-2)}$$

1.8 Electrocatalytic hydrogen evolution reaction testing (1 M KOH)

The reference electrode is Mercury (II) oxide electrode and the counterpart electrode is carbon rod electrode, Electrode cleaning and performance test sections are 1 M KOH solution. Because the reference electrode is Mercury (II) oxide electrode, the final results need to be converted to standard hydrogen electrodes (RHE). The specific calculation formula (S-3) is as follows:

$$E_{(RHE)} = E_{(Hg/HgO)} + 0.098 + 0.059 * pH - 0.9 * iR \qquad \text{(S-3)}$$

2. Electrodeposition of PtRuRhPdAuIr HEA in DES

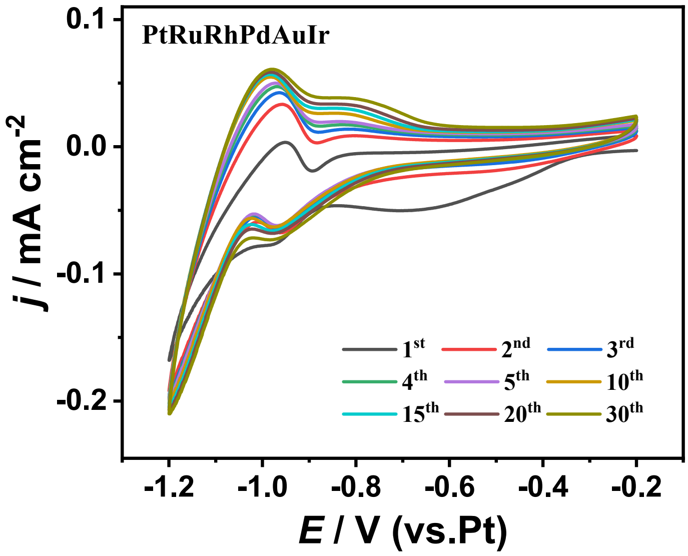

Fig. S1 The different scanning cycles of cyclic voltammograms on GC electrodes in ChCl-urea-based DES containing containing K_2PtCl_6, $RuCl_3$, $RhCl_3$, $PdCl_2$, $HAuCl_3$ and $IrCl_3$ precursors. Scan rate: 50 mV s^{-1}, Temperature: 60 ºC.

3. EDX of PtRuRhPdAuIr HEA

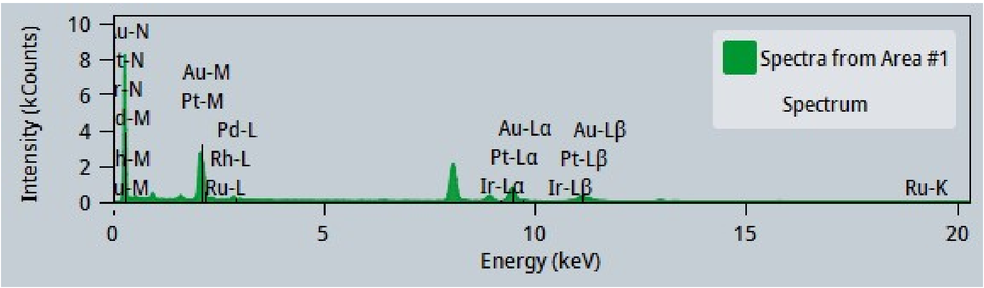

Fig. S2 EDX of PtRuRhPdAuIr HEA.

4. ICP-MS of PtRuRhPdAuIr HEA

Table S1. ICP-MS result of PtRuRhPdAuIr HEA.

Elements	Mass/μg	Molar percentage / %
Pt	6.4470	24
Ru	3.4777	25
Rh	0.2288	1
Pd	3.8504	26
Au	6.0428	22
Ir	0.4727	2

5. XPS spectrum

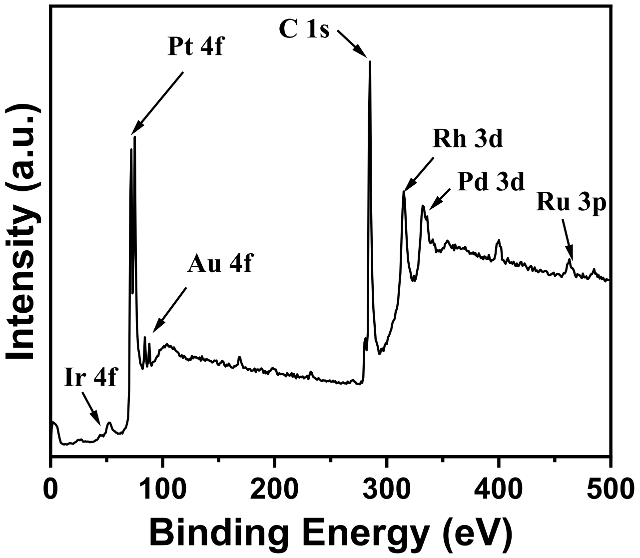

Fig. S3 XPS survey spectrum of PtRuRhPdAuIr HEA.

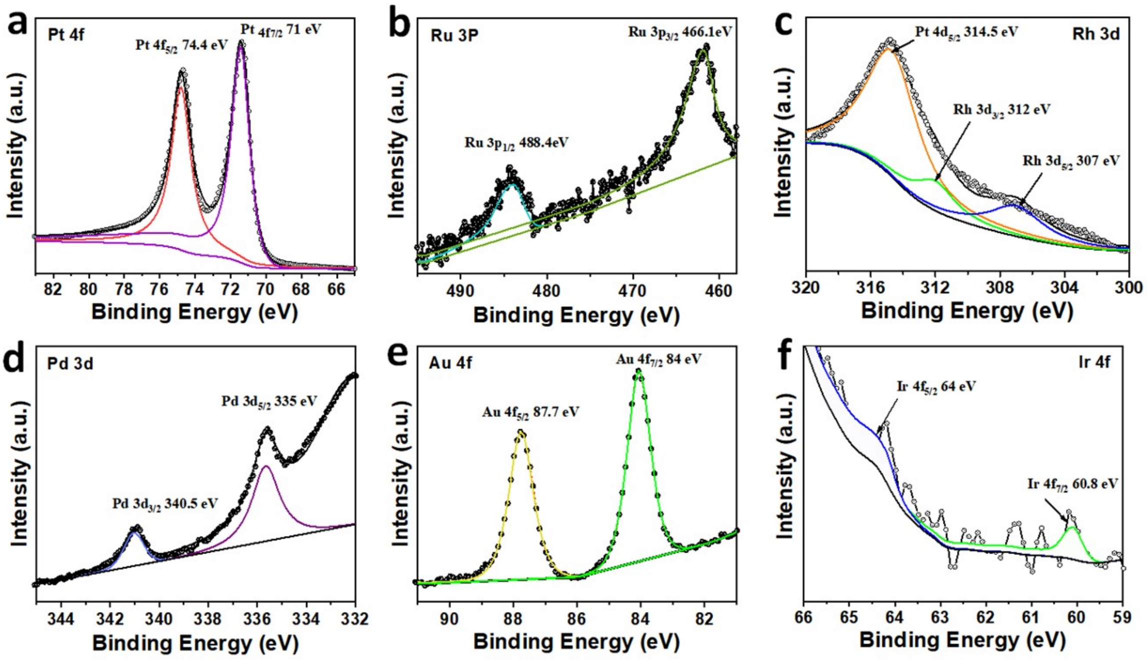

Fig. S4 XPS spectra of PtRuRhPdAuIr HEA: (e) Pt 4f, (a) Ru 3p, (b) Rh 3d, (c)Pd 3d, (d) Au 4f, and (f) Ir 4f.

6. SEM images

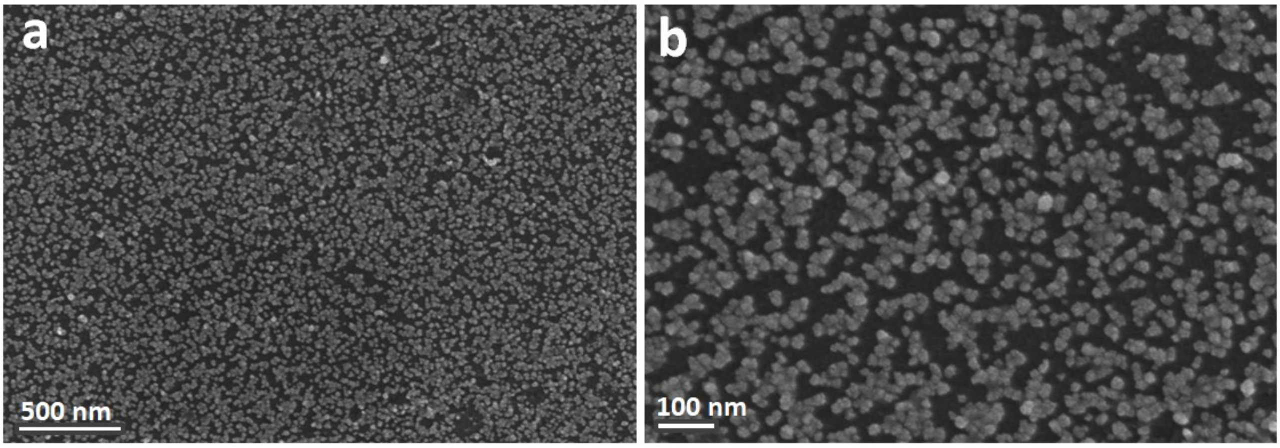

Fig. S5 SEM images of PtRuRhPdIr.

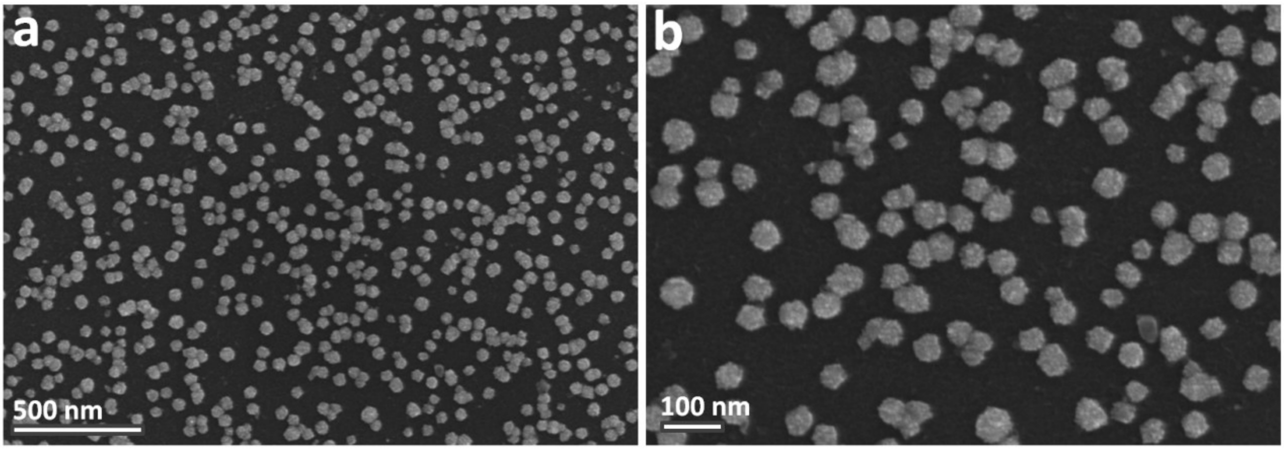

Fig. S6 SEM images of PtRuRhAuIr.

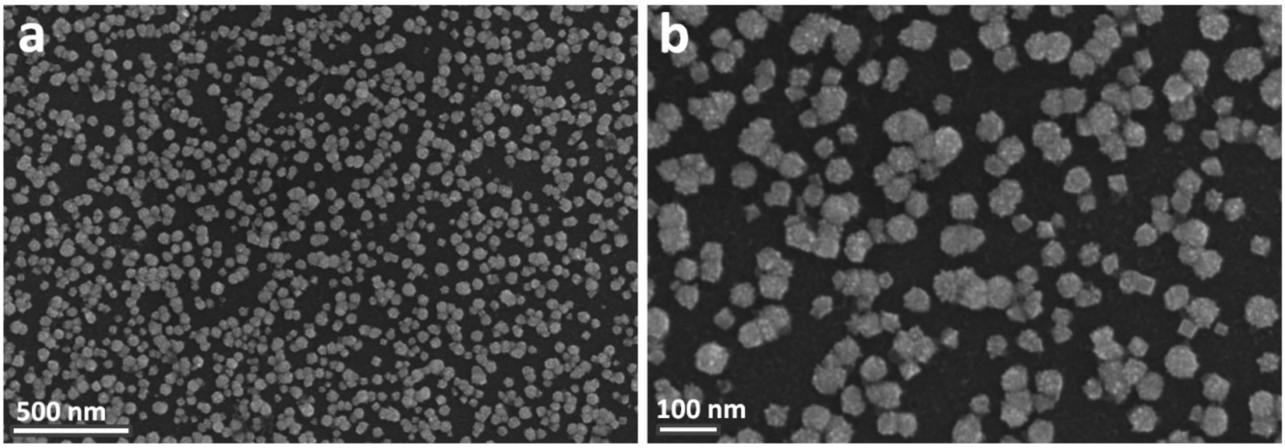

Fig. S7 SEM images of PtRuPdAuIr.

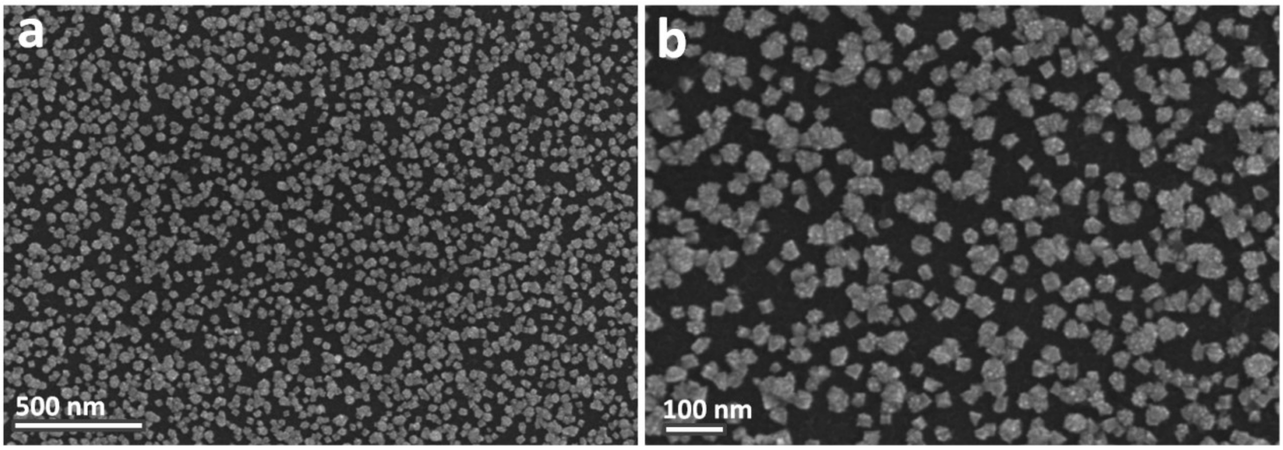

Fig. S8 SEM images of PtRhPdAuIr.

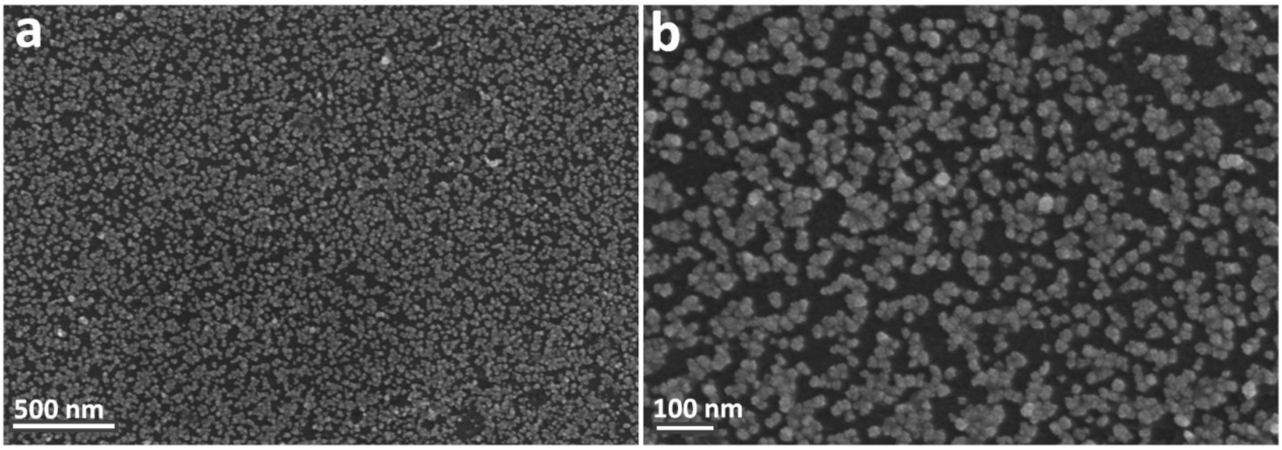

Fig. S9 SEM images of PtRuRhPdIr.

7. CO_{ad} stripping voltammograms

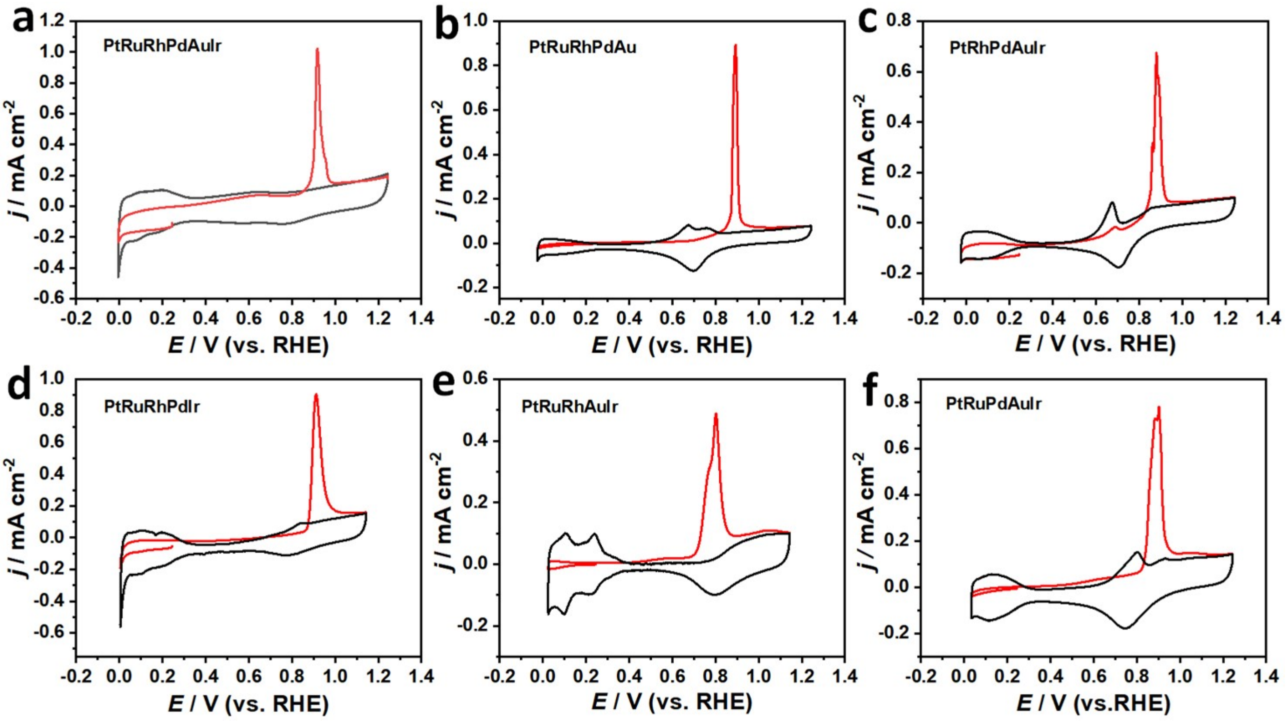

Fig. S10 CO stripping voltammograms: (a) PtRuRhPdAuIr, (b) PtRuRhPdAu, (c) PtRhPdAuIr, (d) PtRuRhPdIr, (e) PtRuRhAuIr, (f) PtRuPdAuIr, were all performed in a 0.5 M H_2SO_4 solution at a scanning rate of 50 mV s^{-1}.

8. Cyclic voltammograms experiment

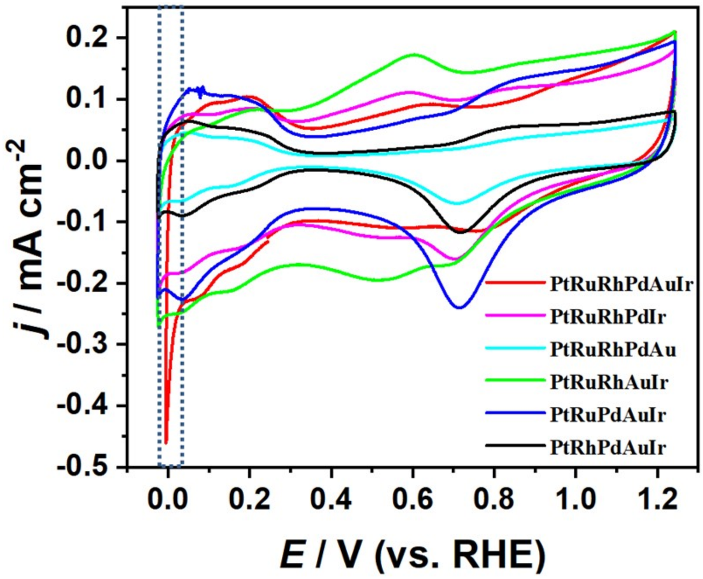

Fig. S11 Cyclic voltammetry curves of PtRuRhPdAuIr HEA and five quinary HEAs in a 0.5 M H_2SO_4 solution, scanning rate: 50 mV s^{-1}.

9. Electrochemical impedance spectroscopy (EIS) measurement in acidic electrolyte

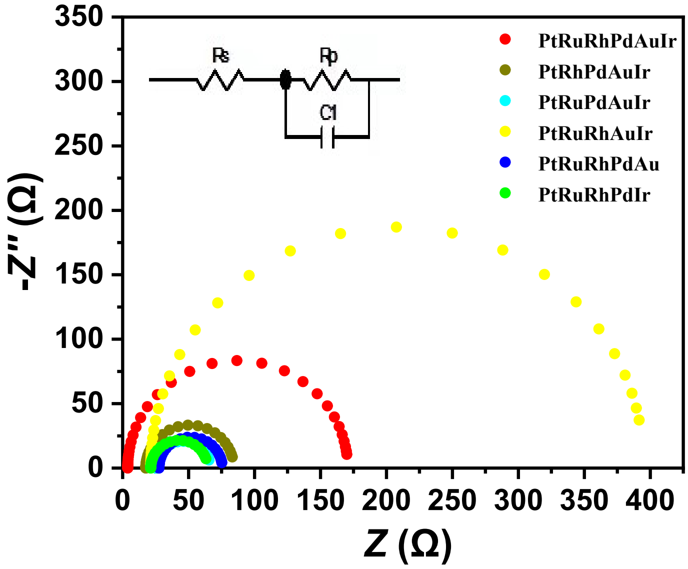

Fig. S12 EIS spectra PtRuRhPdAuIr HEA and quinary alloys in 0.5 M H_2SO_4 solution.

Fig. S12 shows the electrochemical impedance spectroscopy (EIS) of the acanthosphere-like PtRuRhPdAuIr HEA and quinary alloys. It can be seen that the solution internal resistance (R_s) of acanthosphere-like PtRuRhPdAuIr HEA is 4 Ω, which is close to the solution internal resistance of quinary alloys. The charge transfer resistance (R_{ct}) of acanthosphere-like PtRuRhPdAuIr HEA is 83 Ω, and the quinary alloys PtRuRhPdIr, PtRuRhPdAu, PtRuRhAuIr, PtRuPdAuIr and PtRhPdAuIr is 21, 23, 181, 20 and 32 Ω, respectively.

10. Polarization curves with and without iR correction

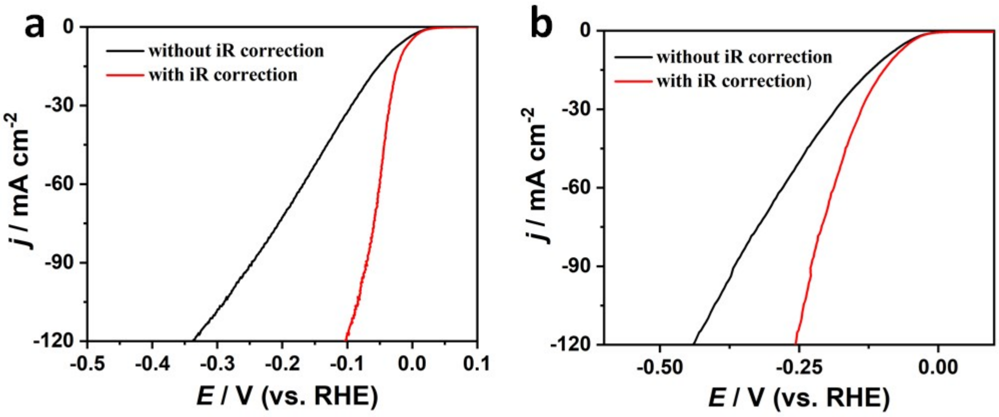

Fig. S13 Polarization curves with and without iR correction of electrocatalytic HER testing in (a) acidic and (b) alkaline media, scanning rate: 5 mV s^{-1}.

11. SEM images of HEA before and after the durability test

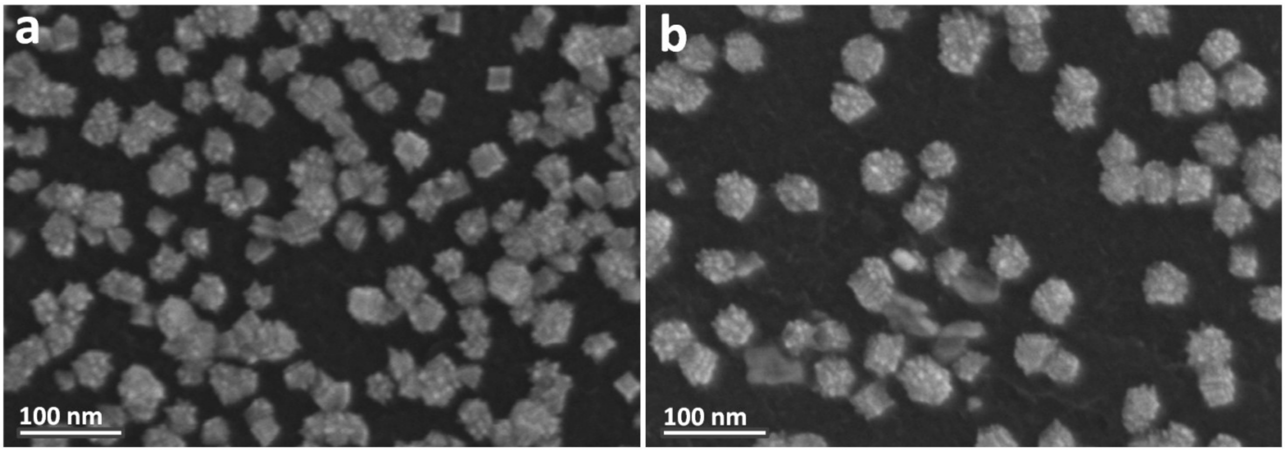

Fig. S14 Comparison of SEM images of PtRuRhPdAuIr HEA: (a) before and (b) after the durability test.

12. Electrochemical impedance spectroscopy (EIS) measurement in alkaline electrolyte

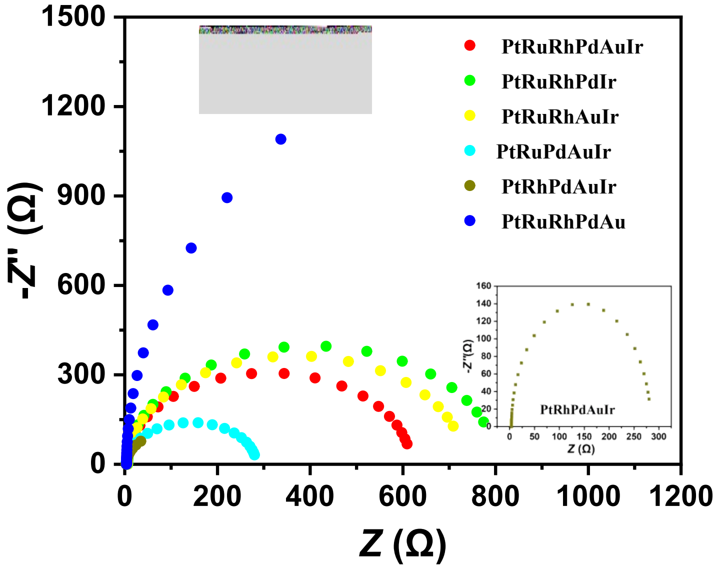

Fig. S15 EIS spectra PtRuRhPdAuIr HEA and quinary alloys in 1 M KOH solution.

Fig. S15 displays the EIS obtained in 1 M KOH solution, indicating that the R_s of as-synthesized acanthosphere-like PtRuRhPdAuIr HEA is 4 Ω, which is close to the R_s of quinary alloys. Notably, the R_{ct} of as-synthesized acanthosphere-like PtRuRhPdAuIr HEA (320 Ω) is much smaller than that of PtRuRhPdIr(400 Ω), PtRuRhAuPd(1500 Ω) and PtRuRhAuIr(390 Ω). However, it is close to PtRuPdAuIr(159 Ω) and PtRhPdIrAu(140 Ω).

References

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