

Electronic Supplementary Information (ESI)

Quinary RuRhPdPtAu high-entropy alloy as an efficient
electrocatalyst for the hydrogen evolution reaction

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1. Experiment

1.1 Materials

Potassium chloroplatinate (K_2PtCl_6 , AR reagent), ruthenium trichloride ($RuCl_3$, GR reagent), rhodium chloride trihydrate ($RhCl_3 \cdot 3H_2O$, AR reagent), palladium chloride ($PdCl_2$, AR reagent), tetrachloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$, AR reagent), urea ($CO(NH_2)_2$, >99%), choline chloride ($HOC_2H_4N(CH_3)_3Cl$, 99%), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, AR reagent), potassium hydroxide (KOH, AR reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). ($HClO_4$, AR reagent) was purchased from Xian Fuchen Chemical Reagent Co., Ltd. (Xian, China). Sulfuric acid (H_2SO_4 , AR reagent) was purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. (Shanghai, China). 5 wt% Nafion solution and 20 wt% Pt/C catalyst was purchased from Sigma-Aldrich and Alfa Aesar, respectively.

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 1:2.¹⁻³ The mixture was heated and stirred in a round bottomed flask at 80 °C until forming a homogenous transparent liquid.

1.3 Preparation of RuRhPdPtAu HEA-NPs

Typically, the RuRhPdPtAu HEA-NPs were prepared by electrochemical cyclic voltammetry (CV) method with scanning potential range between -0.2 and -1.5 V at 50 mV s⁻¹ at 60 °C for 35 cycles in ChCl-U based DES solution containing $RuCl_3$, $RhCl_3$, $PdCl_2$, K_2PtCl_6 , and $HAuCl_3$ precursors. The concentration of each metal

precursor is 24.28 mM. 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, $\Phi = 6$ mm), was polished mechanically by using Al_2O_3 polishing powder with sizes of 1.0 and 0.3 μm , respectively. After electrodeposition, samples were rinsed with ultrapure water and absolute ethanol to remove any residue of the DES, and dry in air before characterization.

1.4 Preparation of monometallic Pt NPs

The control group of monometallic Pt NPs was prepared in a ChCl-U based DES solution containing K_2PtCl_6 of 24.28 mM with other conditions unchanged parameters of HEA.

1.5 Preparation of commercial Pt/C catalyst electrode

The preparation steps are as follows: 5 mg of the commercial Pt/C catalyst and 10 μL Nafion solution (5 wt %) were mixed with 5 mL ultrapure water/absolute ethanol mixed solution (the volume ratio of ultrapure water to absolute ethanol is 1:2), then dispersed by ultrasonic treatment for 10 min. Then take 8 μL of the treated commercial Pt/C catalyst ink drip onto the GCE surface and dried using infrared. The Pt loading of the as-synthesized commercial Pt/C catalyst electrode is 8 μg .

1.6 Characterization

Scanning electron microscopy (SEM) images of RuRhPdPtAu HEA-NPs were 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 RuRhPdPtAu HEA-NPs 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 Ru, Rh, Pd, Pt, and Au content of samples were quantified by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo ICAP-QC).

1.7 Electrochemical surface area

Electrochemical active surface area (ECSA) of the as-synthesized quinary RuRhPdPtAu HEA-NPs was measured by copper under-potential deposition (Cu-UPD) method, which has been described in the previous studies.⁴ Briefly, three CV scans over a range of 0.1–1.5 V (*vs.* RHE) at 50 mV s⁻¹ in N₂-saturated 5 mM H₂SO₄ solution were carried out to clean the working electrode and obtain a background CV curve. Subsequently, the solution was changed to 0.5 M H₂SO₄ + 5 mM CuSO₄. A monolayer of Cu was electrochemically deposited to the working electrode by applying 0.3 V (*vs.* RHE) for 100 s. Immediately after the deposition, the Cu-UPD stripping voltammogram was obtained by scanning the working-electrode voltage over the range of 0.47–0.90 V (*vs.* RHE) at 50 mV s⁻¹. The ECSA of the catalysts was determined under the assumption of 420 μC cm⁻² of Cu²⁺ adsorbed, which can be calibrated as Equation (1):

$$ECSA_{(Cu-UPD)} = \frac{Q_{Cu}}{v \times 420 \mu C \cdot cm^{-2}} \quad (1)$$

where Q_{Cu} (μC) is the charge of Cu-UPD stripping voltammogram, ν is sweep rate ($V s^{-1}$).

The ECSA of monometallic Pt NPs and commercial Pt/C catalyst was determined by the charge of hydrogen adsorption/desorption on Pt surface.⁵ It can be calibrated as Equation (2):

$$ECSA = \frac{Q_H}{\nu \times 210 \mu C \cdot cm^{-2}} \quad (2)$$

where Q_H (μC) the hydrogen adsorption/desorption charge of electrode, ν is sweep rate ($V s^{-1}$).

1.8 Electrocatalytic hydrogen evolution reaction testing

The HER tests were conducted in an H-type electrolytic cell connected to an electrochemical workstation (CHI 760E, Shanghai Chenhua) in 1 M KOH 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 Mercury(II) oxide 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 to -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 30 minutes 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 (vs. RHE) for ohmic potential drop (iR) compensation. Electrochemical impedance spectroscopy (EIS) measurements were tested from 10^5 to 10^{-1} Hz in 1 M KOH 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 Mercury(II) oxide electrode is used, conversion between electrodes is required. The specific calculation formula is as follows:⁶

$$E_{(RHE)} = E_{(Hg / HgO)} + 0.098 + pH * 0.0592 - 0.9 * iR \quad (3)$$

2. Electrodeposition of HEA-NPs from DES

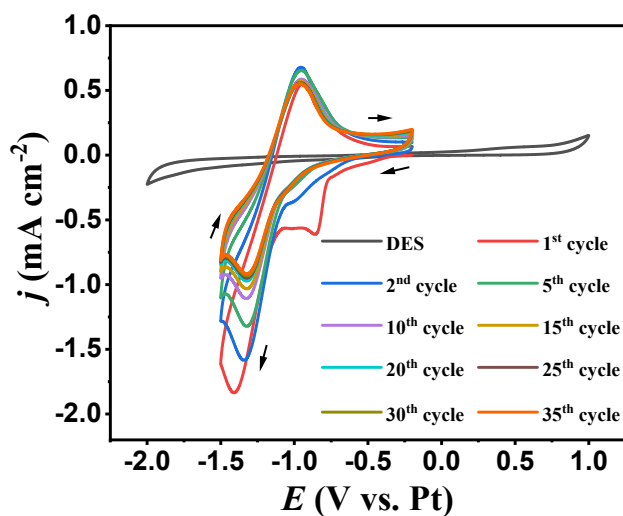


Fig. S1. The different scanning cycles of cyclic voltammograms on GC electrodes in ChCl-urea-based DES containing RuCl_3 , $(\text{NH}_4)_3\text{RhCl}_6$, PdCl_2 , K_2PtCl_6 , and HAuCl_4 (color lines), and pure DES (black line). Scan rate: 50 mV s^{-1} , Temperature: $60 \text{ }^\circ\text{C}$.

Fig. S1 shows CV curves of HEA recorded on GCE in ChCl-U based DES. It clearly reveals a strong reduction peak located in the -1.1 to -1.5 V potential range during the forward scan. Notably, no reduction current was observed in pure DES (black line) in the same potential range, suggesting that the reduction peak is associated with the coreduction process of Ru, Rh, Pd, Pt, and Au precursors from the DES medium. Additionally, it is noteworthy that there is an appreciable oxidation current arisen at the -1.18 to -0.71 V potential range in the backward scan. This peak could be attributed to the oxidation of the surface metal atoms, which can be further reduced during the forward scan soon afterwards.⁵ Furthermore, the reduction peak currents tend to decrease with increasing potential cycle, in agreement with the

previous studies.^{5,7} This change is associated with the decrease of HEA precursors near the electrode surface, which sharply reduced during the first cycle. On the other hand, because the high viscosity of DESs limits the mobility of the reactive species, the precursors in the bulk solution cannot rapidly migrate to the near electrode surface, resulting in a lower concentration of the precursors than the former.

Fig. S2 and Fig. 2a show SEM images of RuRhPdPtAu HEA-NPs electrodeposited by various cycle numbers. The result indicates that the cycle number has a considerable influence on the process of particle growth. When the cycle number is lower, such as 30 cycles, the distribution of the resultant NPs on the electrode surface is very sparse (Fig. S2a). While the cycle number increase to 40 cycles, the resultant NPs seriously agglomerate together to form a film (Fig. S2b). Therefore, the cycle number 35 cycles in between was employed in the typical electrodeposition of RuRhPdPtAu HEA-NPs (Fig. 2a).

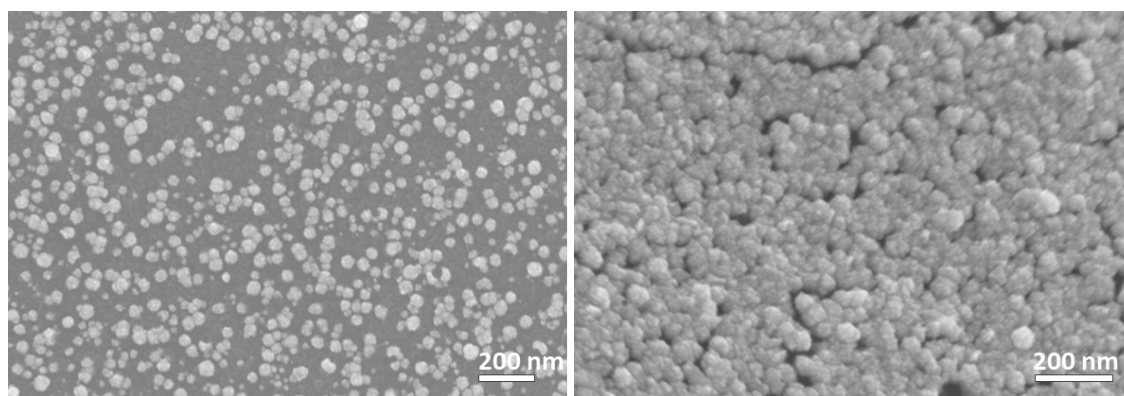


Fig. S2. SEM images of RuRhPdPtAu HEA-NPs electrodeposited by using different cycle number: (a) 30, and (b) 40. Potential scan range: -0.2 and -1.5 V, scan rate: 50 mV s^{-1} .

3. EDX of HEA-NPs

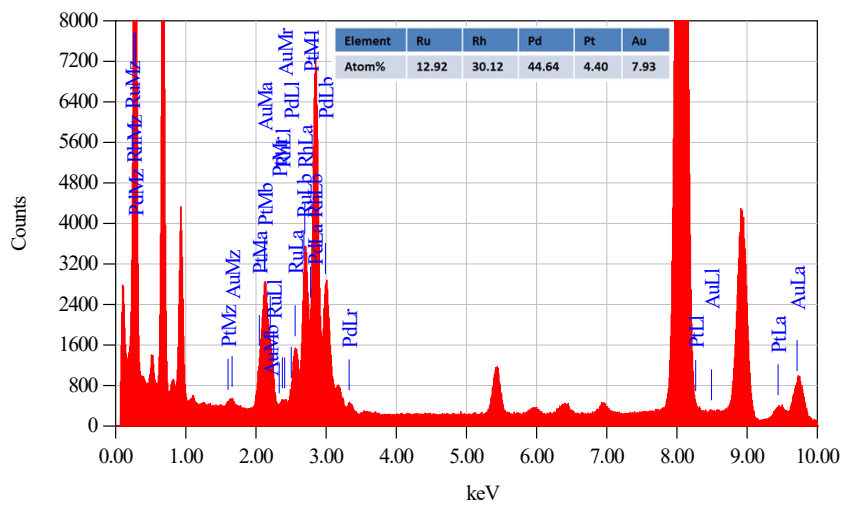


Fig. S3. EDX of as-synthesized RuRhPdPtAu HEA-NPs.

4. ICP-MS of HEA-NPs

Table S1. ICP-MS results of as-synthesized RuRhPdPtAu HEA-NPs.

Elements	Ru	Rh	Pd	Pt	Au	Total
Mass / μg	0.4325	0.8875	0.9925	0.4300	0.8575	3.6
Atom %	15	30	32	8	15	100

5. XPS spectrum of Ru 3p

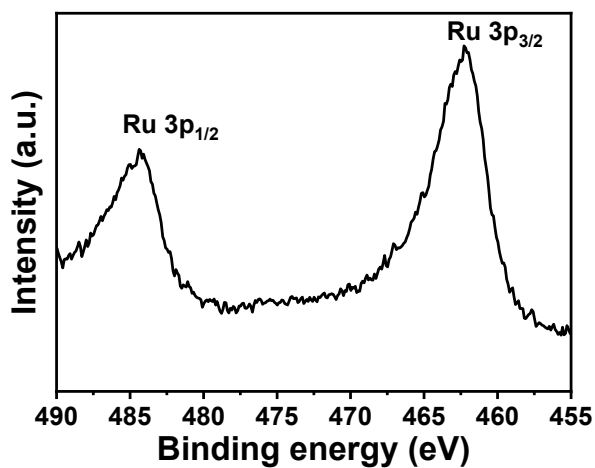


Fig. S4. XPS spectrum of Ru 3p.

6. Copper under-potential deposition

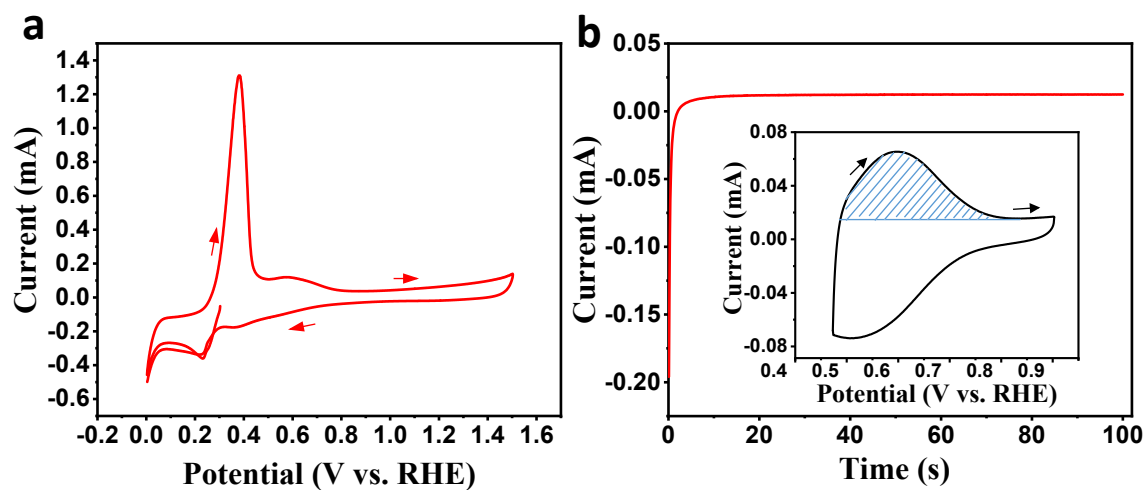


Fig. S5. (a) Cu electrodeposition on RuRhPdPtAu HEA-NPs in 5 mM CuSO₄ + 0.5 M H₂SO₄ solution. Scan rate: 50 mV s⁻¹, Temperature: 25 °C. (b) Cu UPD on

RuRhPdPtAu HEA-NPs.

7. SEM image of monometallic Pt NPs

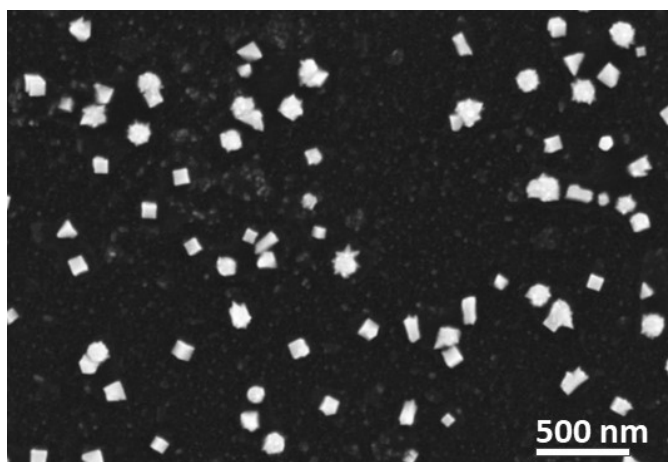


Fig. S6. SEM image of monometallic Pt NPs.

8. SEM image of commercial Pt/C catalyst

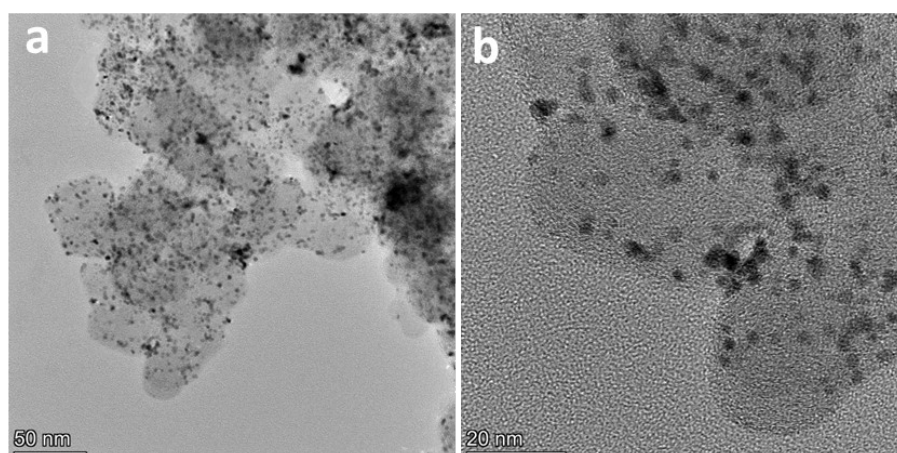


Fig. S7. TEM images of commercial Pt/C catalyst.

9. Cyclic voltammograms experiment

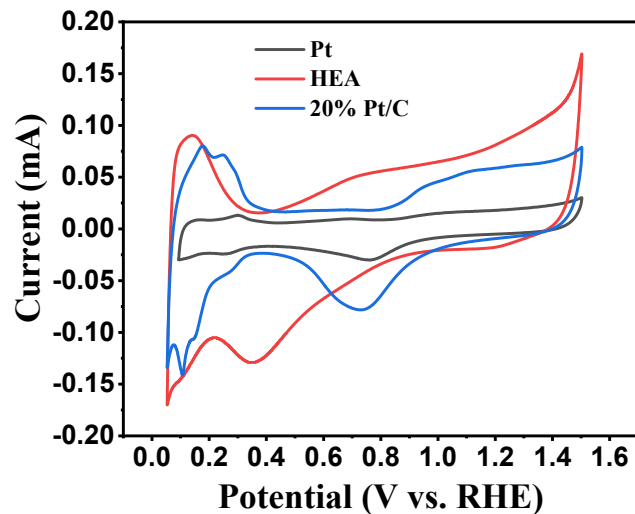


Fig. S8. Cyclic voltammograms on RuRhPdPtAu HEA-NPs, monometallic Pt NPs and commercial Pt/C catalyst in 0.1 M HClO₄ solution. Scan rate: 50 mV s⁻¹, Temperature: 25 °C.

10. EIS experiment

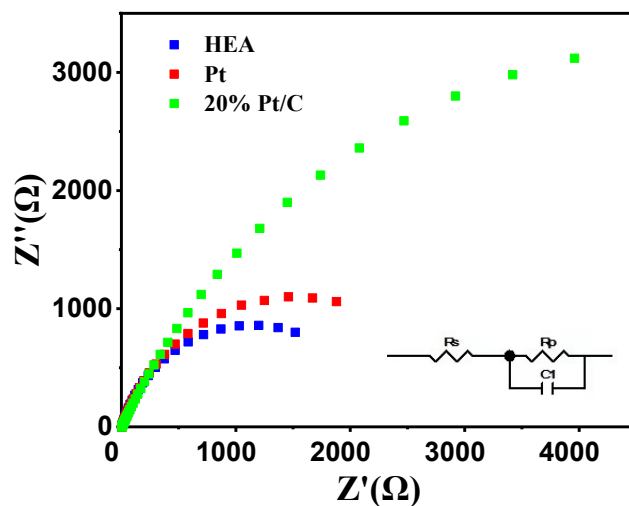


Fig. S9. EIS spectra of RuRhPdPtAu HEA-NPs, monometallic Pt NPs and commercial Pt/C catalyst in 1 M KOH solution. The equivalent circuit is shown in the

inset.

11. Durability of structure and composition for RuRhPdPtAu HEA-NPs

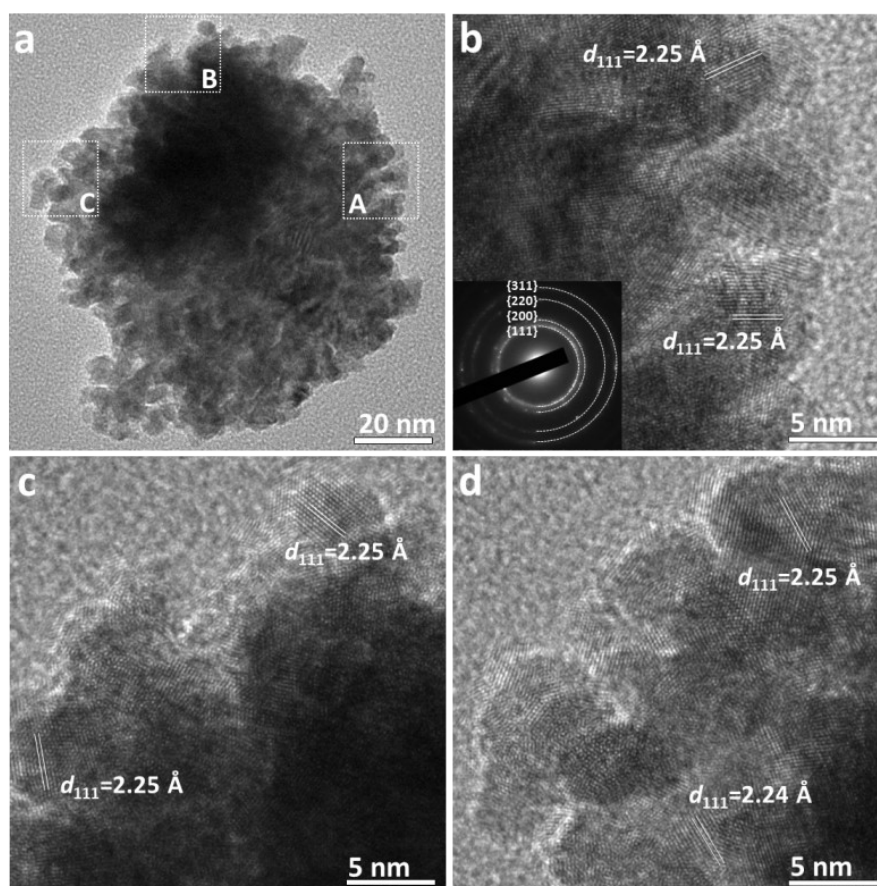


Fig. S10. Structure characterization of RuRhPdPtAu HEA-NPs after the chronoamperometry test. (a) TEM image, (b-d) HRTEM images of (A), (B) and (C) dashed boxes marked in (a).

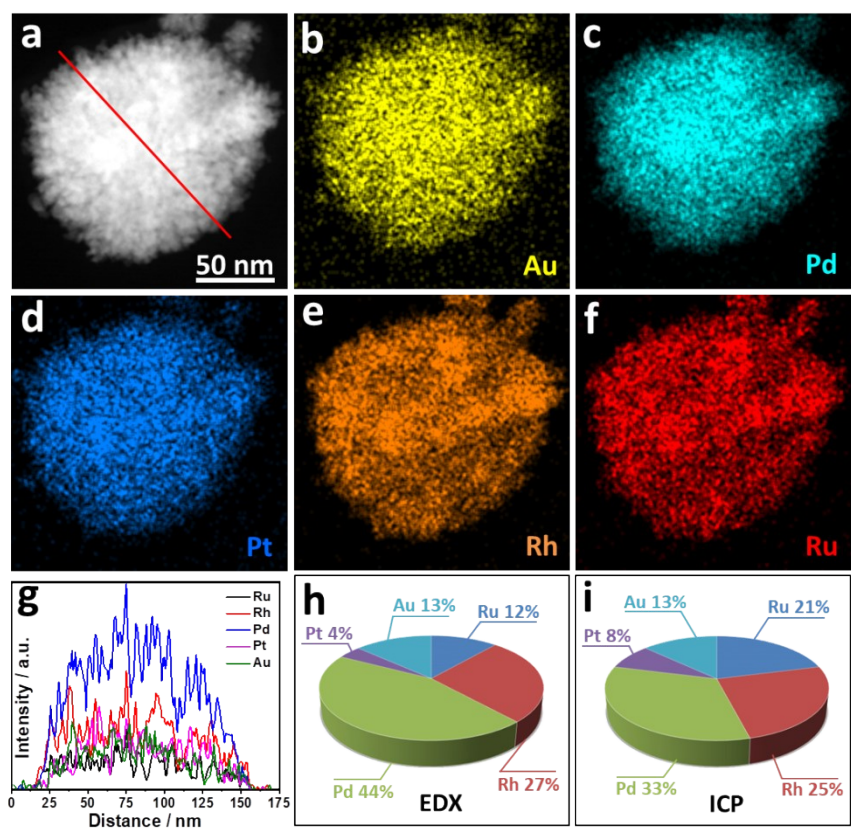


Fig. S11. Composition characterization of RuRhPdPtAu HEA-NPs after the chronoamperometry test. (a-f) HAADF-STEM, EDX mapping images and (g) line scanning profiles of Ru, Rh, Pd, Pt, and Au. (h, i) Metallic compositions obtained by EDX and ICP, respectively.

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