Supplementary Information (SI) for ChemComm.

Supporting Information

Hollow PtPdRhRuCoNi high-entropy alloy as effective electrocatalyst for ethanol, ethylene glycol and glycerol oxidation

Hong Huang,[a] Jia-Lin Li, [a,b] Ai-Jun Wang,[b] Hua-Jie Niu,*[a] Jiu-Ju Feng*[b]

[a] College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, 314001, China

[b] Key laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Materials Science, College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua 321004, China

*Corresponding authors.

Emails: niuhj@zjxu.edu.cn (H.J. Niu); jjfeng@zjnu.cn (J.J. Feng).

Experimental

1. Materials and chemicals

Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), palladium chloride ($PdCl_2$), rhodium chloride ($RhCl_3$), and commercial platinum black were purchased from Shanghai Aladdin Chemical Co. nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), concentrated hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ruthenium chloride ($RuCl_3$) and surfactant Pluronic F127 were purchased from Sigma-Aldrich. Ascorbic acid (AA) was purchased from Macklin Biochemical Co.

2. Preparation of hollow PtPdRhRuCoNi HEA

Typically, an aqueous solution was first prepared by dissolving 0.1 g of the surfactant Pluronic F127 in 3 mL of deionized water under vigorous stirring until a clear solution was obtained. Then, 0.06 mmol each of $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $RhCl_3$ and $RuCl_3$ was added sequentially and stirred until completely dissolved. Subsequently, the following solutions were added in order: 3.1 mL of $H_2PtCl_6{\cdot}6H_2O$ (19.4 mM), 3.0 mL of H_2PdCl_4 (20.0 mM), 4.0 mL AA (0.1 M) and 0.4 mL HCl (6.0 M). The resulting homogeneous mixture was kept at 95 °C in an oil bath for 4 h. Following cooling to room temperature, the product was washed with ethanol and water, and subsequently subjected to dropwise etching with concentrated nitric acid for 24 h to obtain the nano-prismatic hollow spherical PtPdRhRuCoNi high-entropy alloy.

3. Material characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) measurements were taken on a JEM-2100F microscope operating at an acceleration voltage of 200 kV. The elemental mappings were acquired on the scanning transmission electron microscope with a high-angle annular dark-field (HAADF-STEM) detector operated at 30 kV (HITACHI S-5500). The chemical compositions were examined by energy dispersive spectroscopy (EDS) with Vantage Digital Acquisition Engine (Thermo Noran, USA). X-ray diffraction (XRD) experiments were performed on a Bruker-D8-AXS diffractometer equipped with Cu Kα radiation (Bruker Co., Germany). X-ray photoelectron spectroscopy (XPS) measurements were conducted on the K-Alpha XPS spectrometer (ThermoFisher, E. Grinstead, UK) with the Al Kα X-ray radiation (1486.6 eV).

4. Electrochemical experiments

For the electrochemical measurements, a catalyst ink was prepared by dispersing 3 mg of PtPdRhRuCoNi (3 mg mL^{-1}) powder in a mixture of 0.5 mL of ethanol, 0.44 mL of deionized water and 0.06 mL of Nafion (0.5%) via sonication. Then, the catalyst ink (3 μL) was loaded by drop-casting onto a freshly polished glassy carbon electrode (GCE, 3 mm diameter) and dried at ambient temperature. For comparison, an electrode modified with commercial platinum black was fabricated following the same procedure.

All of the electrochemical experiments were performed at a CHI 1030a 3 electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China). Herein, a traditional three-electrode system was employed, in which a saturated calomel electrode (SCE) worked as the reference electrode, a platinum wire as the counter electrode, and a modified glassy carbon electrode (GCE, $\Phi = 3$ mm) as the working electrode. The current density was normalized by the geometrical area of the GCE.

All of the potentials, measured against the SCE, were converted into the potential versus (vs.) reversible hydrogen electrode (RHE) according to the below equation:

$E_{RHE}=E_{SCE}+0.059pH+0.241$

The electrochemical active surface area (ECSA) of the catalyst was calculated by cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} in a 1.0 M KOH solution by the follow-up formula:

$ECSA=Q_A/(C\times m)$

where Q_A is the quantity of the charges required for the reduction of the metal oxides such as Pt in micro-coulomb (μC), C is the proportionality constant, assuming 210 μC cm^{-2} for the reduction of a monolayer Pt on the catalyst surface, and represents the mass of the Pd loading on the electrode.

The cyclic voltammetry (CV) measurements were conducted at 50 mV s^{-1} in the 1.0 M KOH electrolyte containing 1.0 M ethylene glycol or glycerol. The chronoamperometry (CA) tests were carried out by applying the potentials of 0.628 V, 0.738 V and 0.698 V for ethylene ethanol, glycol and glycerol oxidation, respectively. All of the experiments were performed at room temperature if not stated otherwise.

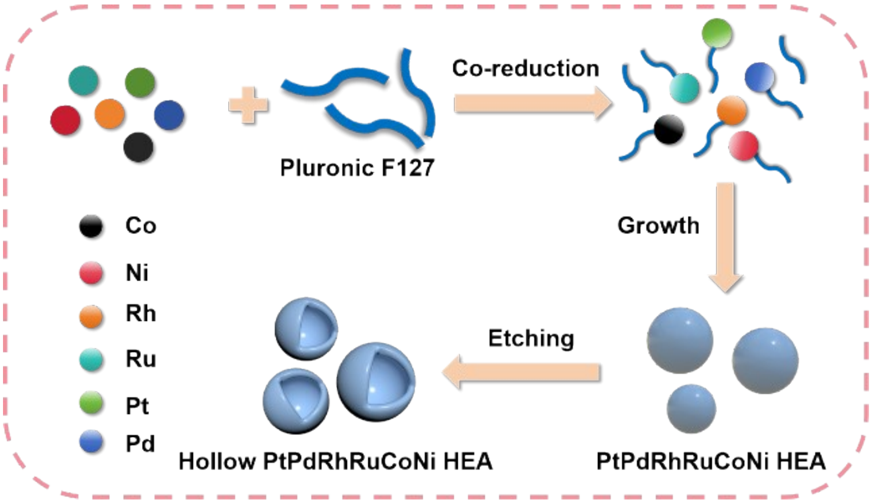

Fig. S1 Scheme for preparation of hollow PtPdRhRuCoNi HEA.

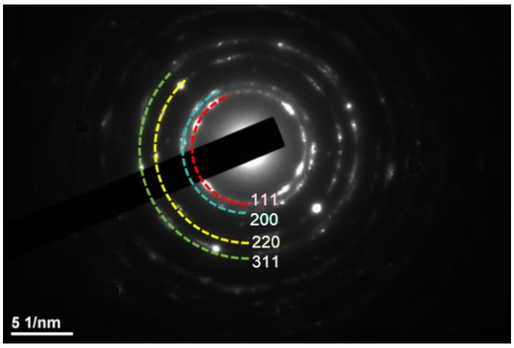

Fig. S2 SAED pattern of hollow PtPdRhRuCoNi HEA.

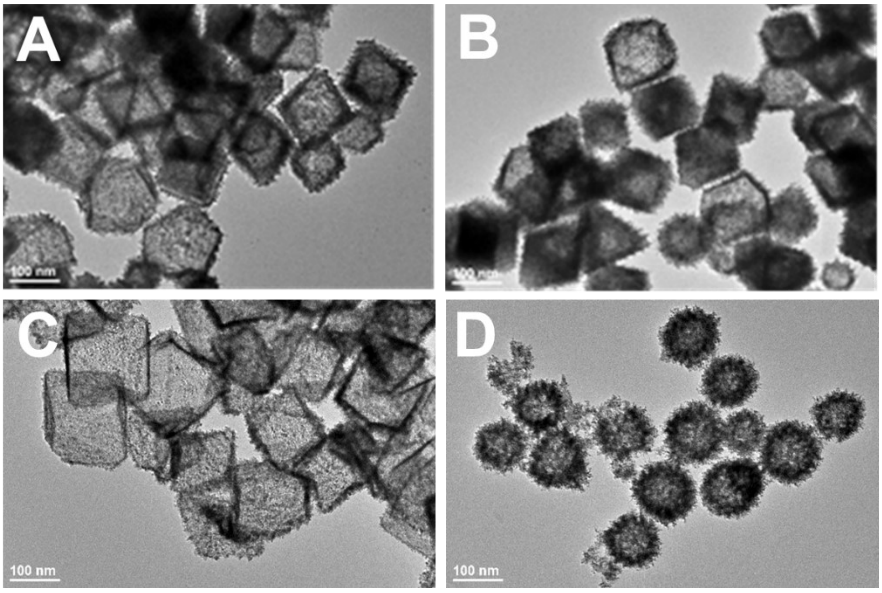

Fig. S3 The TEM image of (A) PtPdCoFeMn, (B) PtPdRuMnNi, (C) PtPdCoRuFe, and (D) PtPdCoRhCu HEA prepared using the proposed strategy.

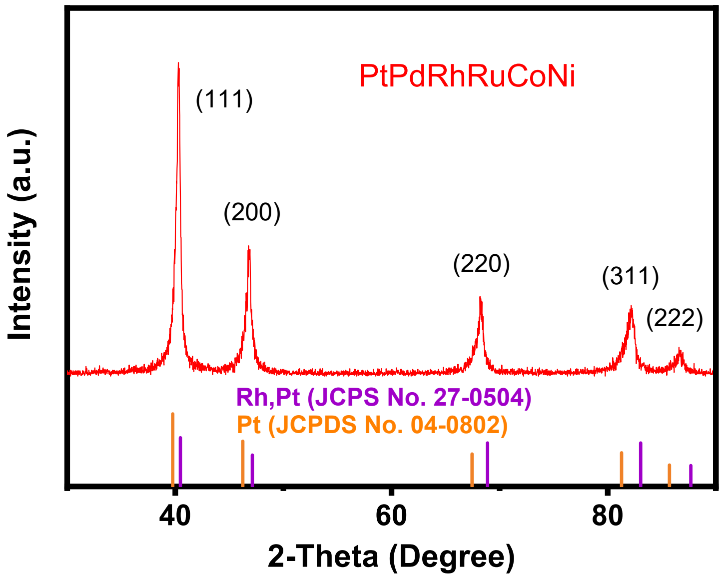

Fig. S4 XRD pattern of PtPdRhRuCoNi HEA.

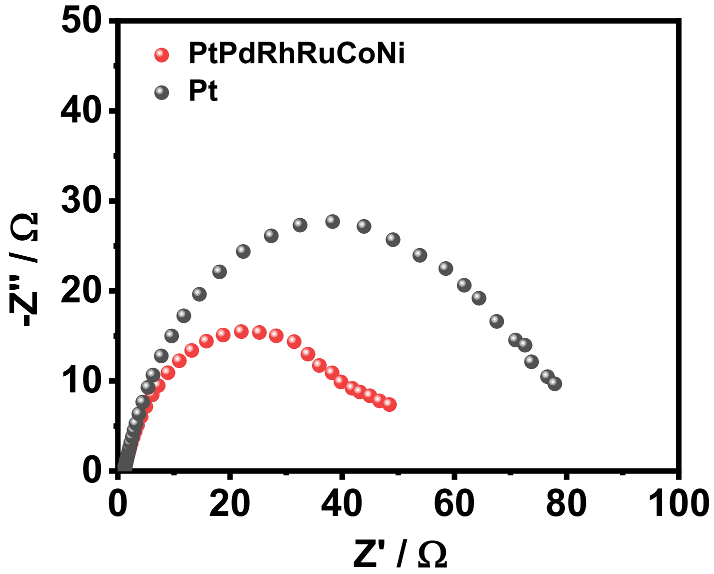

Fig. S5 The EIS curves of PtPdRhRuCoNi HEA and Pt black catalysts 1.0 M KOH.

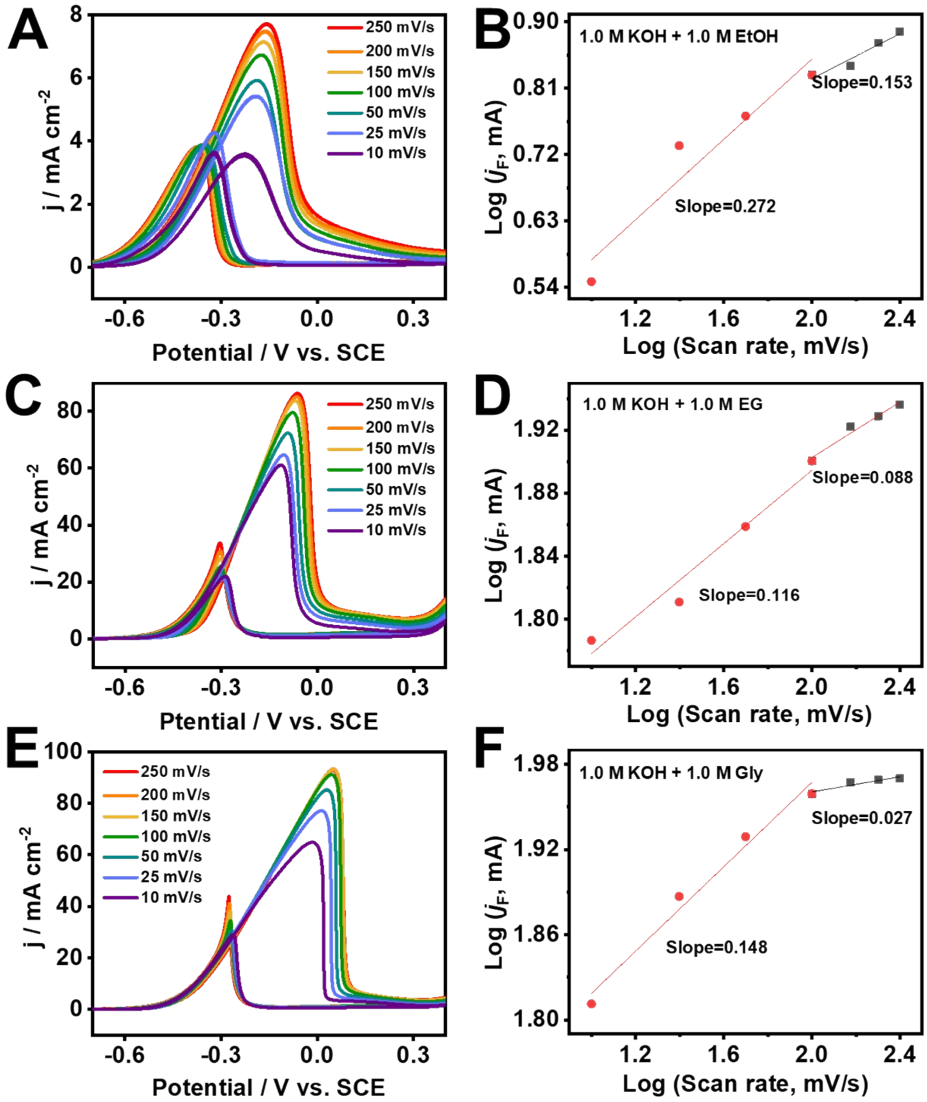

Fig. S6 A series of CV curves at various scan rates and calculated b-value of the forward peak currents at scan rate of 10 to 250 mV s^{-1} of PtPdRhRuCoNi HEA catalyst in (A, B) 1.0 M KOH + 1.0 M EtOH, (C, D) 1.0 M KOH + 1.0 M EG and (E, F) 1.0 M KOH + 1.0 M Gly.

In the low scan rate (10-100 mV s^{-1}), the process is predominantly governed by limiting diffusion control. As the scan rate increases (100-250 mV s^{-1}), charge-transfer interface reaction kinetics become the main controlling factor.

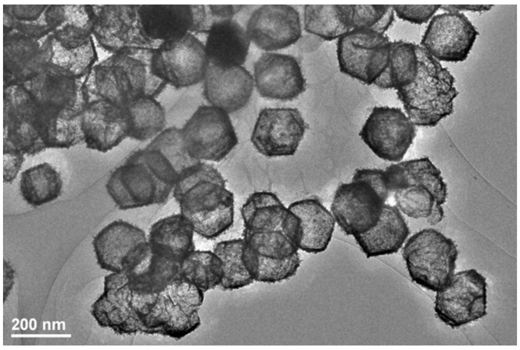

Fig. S7 TEM image of hollow PtPdRhRuCoNi HEA after long-term electrochemical test.

Table S1. The metal contents of PtPdRhRuCoNi HEA by ICP-MS analysis before and after long-term electrochemical test.

	Pt (%)	Pd (%)	Rh (%)	Ru (%)	Co (%)	Ni (%)
Initial	36.6	9.7	28.9	13.4	6.3	5.1
After long-term test	37.1	9.5	28.5	13.5	6.5	4.9

Table S2. Comparison of the catalytic data of the PtPdRhRuCoNi HEA with Pt black catalyst for ethanol, glycol and glycerol oxidation.

Catalysts	**Alcohols**	**j_f/mA cm^{-2}**	**E_{onset}/V**
PtPdRhRuCoNi	ethanol	6.55	0.38
	glycol	72.96	0.48
	glycerol	85.43	0.28
Pt black	ethanol	2.52	0.42
	glycol	15.43	0.53
	glycerol	8.50	0.51

Table S3. Comparison of the PtPdRhRuCoNi HEA for EGOR in the alkaline conditions with other previous catalysts.

Catalysts	Electrolytes	MA	References
Pd_3Pb MAs	1.0 M KOH+0.5 M EG	1.63 A $mg^{-1}{}_{Pd}$	[1]
Pd_3Sn MAs	1.0 M KOH+0.5 M EG	1.69 A $mg^{-1}{}_{Pd}$	[2]
Pd@PdOs NBs	1.0 M KOH+1.0 M EG	1.45 A $mg^{-1}{}_{Pd}$	[3]
$Pd\text{-}Ni(OH)_2$	1.0 M KOH+1.0 M EG	0.8 A $mg^{-1}{}_{Pd}$	[4]
PtPdRhRuCoNi	**1.0 M KOH+1.0 M EG**	**1.71 A $mg^{-1}{}_{Pt+Pd}$**	**This Work**

References

[1] H. Fu, Z. Huang, T. Zhu, L. Guan, C.-W. Pao, W.-H. Huang, N. Zhang, T. Liu, Low-coordinated Pd–Pb sites in porous Pd_3Pb metallene aerogels promote polyalcohol electrochemical oxidation, ACS Materials Letters, 6 (2024) 4801-4809.

[2] L. Guan, H. Fu, T. Zhu, C. Chen, Z. Zhang, Y. Pi, N. Zhang, T. Liu, p–d orbital hybridization in Pd_3Sn metallic aerogels boosts alcohol electrooxidation, Chem Mater, 36 (2024) 9741-9749.

[3] X. Wang, X. Wei, R. Zhang, M. Yan, R. Wei, X. Zhang, Z. Zhu, Y. Wang, X. Zhao, S. Yin, Defect-rich Pd@PdOs nanobelts for electrocatalytic oxidation of ethylene glycol, Inorganic Chemistry Frontiers, 11 (2024) 2562-2569.

[4] F. Liu, X. Gao, R. Shi, Z. Guo, E.C.M. Tse, Y. Chen, Concerted and selective electrooxidation of polyethylene-terephthalate-derived alcohol to glycolic acid at an industry-level current density over a $Pd{-}Ni(OH)_2$ catalyst, Angewandte Chemie International Edition, 62 (2023) e202300094.