Electronic Supplementary Information for

Rapid co-reduction synthesis of ultrafine multi-principal

element alloy nanocatalysts for efficient hydrogen evolution

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Experimental section

Chemicals.

Anhydrous stannous chloride (SnCl₂), copper chloride dihydrate (CuCl₂·2H₂O) and potassium pentachloro-nitrosoruthenate (K₂Ru(NO)Cl₅) were purchased from Aladdin. Platinum acetylacetonate (Pt(C₅H₇O₂)₂) was purchased from Alfa Aesar. Aluminum chloride hydrate (IrCl₃·xH₂O) was purchased from TCI. Triethylene glycol and ethylene glycol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial Pt/C (20%) was purchased from Premetek Co.

Synthesis of multi-principal element alloy (MPEA) nanocatalysts

Firstly, the metal precursors $K_2Ru(NO)Cl_5$, $Pt(C_5H_7O_2)_2$, $IrCl_3-xH_2O$, $CuCl_2-2H_2O$ and $SnCl_2$ were added to 0.03 mmol and 10 mL triethylene glycol respectively, and the precursor A solution was ultrasonic until completely dissolved. Next, solution B is made by dispersing an appropriate amount of carbon black carrier in 100 ml glycol, and then the solution B was placed in an oil bath at 180 °C, and maintained at the same temperature. Then the precursor A solution was added into the B solution. After 10 min reaction, the reaction mixture is promptly cooled to room temperature using an ice bath. Finally, the products were collected, centrifuged (8000 rpm, 5 min), and washed with acetone and ethanol twice. After the last centrifugation, the sample is dried in a 60 °C oven to obtain a binary and MPEA.

Characterizations

Powder X-ray diffraction (XRD) data was recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA with scanning rate of 0.02° per step. The diffraction patterns were recorded in the range of 10-80° 20. The inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted on an Aglient 5110. High-Resolution Transmission Electron Microscopy (HRTEM) characterization was performed on a ThermoFisher Talos F200X microscope under 200 kV a ThermoFisher Themis Z microscope under 300 kV. High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors.

Electrochemical measurements

All electrochemical measurements were performed on CHI 660E electrochemical workstation under a standard three-electrode system. A graphite electrode, a saturated calomel electrode (SCE) and glassy carbon were used as the counter electrode, reference electrode, and working electrode, respectively. The configuration of the catalyst ink is to add 5 mg catalyst and 60 μ L 5 % Nafion solution to 800 μ L ethanol and 200 μ L deionized water, and ultrasonic treatment for 2 h to obtain. Then, 20 μ L catalyst ink was uniformly dropped on the smooth surface of the glassy carbon electrode and dried naturally to prepare the working electrode. The linear sweep voltammetry (LSV) method was used to test the hydrogen evolution reaction (HER) activity of the catalyst in nitrogen-saturated 0.5 M H₂SO₄ electrolyte with a scan rate of 5 mV/s. All potentials were referenced to reversible hydrogen three electrode (RHE) by following calculations:

$$Evs._{RHE} = Evs._{SCE} + 0.059 \times pH + 0.224$$

The polarization curves were corrected by IR compensation, The correction was performed according to the following calculations:

$$E_{corrected} = E_{measured} - iR_{s}$$

where E is the potential and i is the current flowing through the system. Many electrochemical workstations can measure the value of R directly. Long-term stability tests were carried out by taking 5000 cyclic voltammetry (CV) tests at a scan rate of 200 mV/s in nitrogen-saturated 0.5 M H_2SO_4 .

Commlag	Chemical composition wt %				
Samples	Pt	Ru	Ir	Sn	Cu
RuPt/C	4.7	4.5	-	-	-
RuPtIr/C	4.1	1.6	5.1	-	-
RuPtIrSn/C	3.8	1.6	2.8	0.51	-
RuPtIrSnCu/C	3.8	2.4	1.9	1.8	0.64

 Table S1. Chemical compositions of MPEA catalysts from ICP-OES

Samples	d (111)
RuPt	2.112 Å
RuPtIr	2.113 Å
RuPtIrSn	2.161 Å
RuPtIrSnCu	2.162 Å

Table S2. Lattice spacings of the FCC (111) planes of MPEA

Synthetic method	Material	Characteristic	Ref.
Carbothermal shock	PtPdRhRuCe	Carbothermal shock is a method for synthesizing specific nanomaterials through rapid and drastic temperature changes within an extremely short period of time, such as milliseconds. This method has the advantages of high catalyst preparation efficiency. However, it is not conducive to widespread use due to the need for specialized equipment and professional operators. Additionally, the difficulty in controlling process parameters hinders the precise structural regulation of the catalyst.	1
Laser ablation	CoCrFeMnNi	Laser ablation refers to the process of utilizing the interaction between laser and matter to mix and reduce multiple metal elements through rapid heating, melting, and cooling. Laser ablation for the preparation of MPEA catalyst boasts advantages such as high precision, high efficiency, and uniform composition. However, it also has drawbacks including high equipment costs, difficult control of process parameters, relatively low preparation efficiency, and safety risks.	2
Sputtering	CrMnFeCoNi	Sputtering is commonly used for preparing thin film catalysts of MPEA. The sputtering method boasts advantages such as precise composition control, high film quality, ease of preparing complex structures, and process flexibility. However, it also has drawbacks including high equipment costs, low preparation efficiency, challenges in achieving uniform composition, high energy consumption, and safety risks.	3
Fast moving bed pyrolysis	FeCoPdIrPt	Fast moving bed pyrolysis utilizes a rapidly moving bed layer to achieve an efficient and continuous pyrolysis process. The preparation of high-entropy alloys using a fast moving bed pyrolysis method	4

Table S3. Different synthesis methods of MPEA and their characteristic
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	boasts advantages such as continuous	
	production, uniform composition, process	
	flexibility, and high raw material	
	utilization. However, it also has drawbacks	
	including complex equipment, high energy	
	consumption, limited preparation	
	efficiency, difficulty in controlling	
	composition, and safety risks.	
	The rapid co-reduction method refers to a	Rapid Co- reduction RuPtIrSnCu synthesis
	simple, convenient, and efficient	
	preparation technique for synthesizing	
	multicomponent alloys by rapidly reducing	
Т	pre-mixed and uniformly dispersed metal	
	precursors using ethylene glycol as a	
W	strong reducing agent. This method does	
	not rely on expensive and specialized	
	equipment or professional operators, and	
	can be completed under basic chemical	
	laboratory conditions.	

	Before ADT		After ADT	
Sample	Overpotential	Tafel	Overpotential	Tafel
	(mV)	(mV/dec)	(mV)	(mV/dec)
Pt/C	26	34	36	43
RuPt/C	20	21	24	23
RuPtIr/C	25	25	32	28
RuPtCu/C	25	27	28	29
RuPtSn/C	21	27	24	30
RuPtIrSn/C	18	20	20	27
RuPtIrCu/C	23	28	25	30
RuPtSnCu/C	16	19	20	23
RuPtIrSnCu/C	13	19	18	22

Table S4. The electrochemical performance of all MPEA nanoparticle catalystsbefore and after ADT.

Material	Applications	Activity	Ref.	
NiCoFePtRh nanoparticles		27 mV @ 10 m A /sm2	5	
(5 wt %)	HER IN 0.3 M H_2SO_4	27 mv @ 10 mA/cm ²	3	
PtPdRhRuCu mesoporous		12 my @ 10 m \ /om ²	6	
nanospheres (28 wt %)	$\mathbf{HEK} \ \mathbf{III} \ 0.3 \ \mathbf{M} \ \mathbf{H}_2 \mathbf{SO}_4$			
PdMoGaInNi nanosheets		$12 \text{ mV} \oplus 10 \text{ m} \text{ A/sm}^2$	7	
(20 wt %)	HER IN 0.3 M H_2SO_4	13 m v @ 10 mA/cm ² ;	/	
RuPtIrSnCu nanoparticles		13 mV @ 10 mA/cm ²	This	
(10 wt %)	HEK IN 0.3 M H_2SO_4	19 mV/dec^1	work	

Table S5. MPEA were synthesized by various methods for acidic HER reaction.



Figure S1. TEM images and particle size distribution of (a) RuPt/C, (b) RuPtIr/C, (c) RuPtIrSn/C, and (d) RuPtIrSnCu/C nanocatalysts.



Figure S2. TEM images of MPEA nanocatalysts. (a) RuPtCu/C, (b) RuPtSn/C, (c) RuPtIrCu/C, and (d) RuPtSnCu/C.



Figure S3. HRTEM images and corresponding FFT patterns of (a) RuPtCu/C, (b) RuPtSn/C, (c) RuPtIrCu/C, and (d) RuPtSnCu/C alloy nanocatalysts.



Figure S4. HAADF-STEM images and corresponding EDS elemental maps of MPEA nanocatalysts. (a) RuPtCu/C, (b) RuPtSn/C, (c) RuPtIrCu/C, and (d) RuPtSnCu/C.



Figure S5. TEM characterization of RuPtIrSnCu/C obtained via prolonged reaction time to 1h. (a) HAADF-STEM image and the EDS maps. (b) Overview TEM image.



Figure S6. CV curves for (a) RuPt/C, (b) RuPtIr/C, (c) RuPtIrSn/C, and (d) RuPtIrSnCu/C before and after 5000 cycles in 0.5 M H₂SO₄.



Figure S7. Electrochemical evaluation of the as-prepared other MPEA catalysts. (a) Tafel plots before and (b) after 5000th cycles of the ADT test in 0.5 M H_2SO_4 . (c) Overpotentials at 10 mA/cm² and (d) LSV curves of other MPEA catalysts before and after 5000th cycles of the ADT test in 0.5 M H_2SO_4 .

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