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Recent Advances in High-Entropy Intermetallic Nanoparticles: Synthesis and Electrocatalytic Applications

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High-entropy intermetallics (HEIs) are a novel class of materials that combine the ordered atomic structure of traditional intermetallic compounds with the compositional complexity of high-entropy alloys. This unique combination endows HEIs with exceptional stability and tunable electronic structures, making them promising candidates for advanced catalytic applications. Currently, most reports on HEIs focus on bulk materials, studies on HEI nanoparticles (NPs) remain relatively limited. This review provides an overview of the recent advances in HEI NPs, including their synthesis methods and applications in electrochemical catalysis. First, we introduce the key characteristics of HEIs, focusing on their unique combination of ordered atomic structure and compositional complexity. We then summarise the synthesis methods for HEI NPs reported in recent years. Finally, representative examples are provided to illustrate the application of HEI NPs in electrochemical catalytic reactions such as hydrogen evolution, formic acid oxidation, and oxygen reduction reactions. This review aims to offer insights into the future directions of HEI and promote innovation in both synthesis methods and practical applications of HEI NPs.

1. Introduction

Environmental and energy challenges are becoming increasingly critical globally. The excessive consumption of fossil fuels increases the risk of resource depletion and causes serious environmental pollution and climate change. Given this background, developing efficient and sustainable energy conversion technologies to address these global challenges is critical. Electrochemical catalytic reactions play a crucial role in the development of sustainable energy technologies. For example, in water electrolysis, the oxygen evolution reaction (OER) at the anode generates O₂, while the hydrogen evolution reaction (HER) at the cathode produces H₂.^[1,2] Alcohols (e.g. methanol and ethanol) and formic acid molecules can be

utilised as fuels in direct alcohol fuel cells (DAFC) and formic acid fuel cells (DFAFC),^[3] respectively, and are oxidised to CO₂ at the anode. Meanwhile, the fuel cell cathode undergoes an oxygen reduction reaction (ORR), in which oxygen is reduced to water.^[4] Additionally, the electrochemical nitrate reduction reaction (NO₃RR) offers an environmentally friendly and sustainable pathway for ammonia (NH₃) production.^[5] However, some electrochemical reactions, such as the ORR and HER, involve complex electron transfer processes^[6–8], which result in lower reaction rates and require higher energy inputs. Therefore, catalysts are crucial in electrochemical reactions because they can lower the activation energy, thereby accelerating the reaction rate and increasing energy conversion efficiency.^[9,10]

Noble metals, particularly platinum group metals (PGMs), are commonly used as electrocatalysts. For example, Pt is the most effective catalyst for HER and ORR.^[11,12] However, the

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Megumi Mukoyoshi graduated from Kyoto University in 2014 (MSc, Chemistry), after which she worked as a researcher at Showa Denko K. K. (2014–2017) and Daikin Industries, Ltd. (2018–2021). On her return to Kyoto University, she obtained her PhD (2022), and was later appointed Assistant Professor. Her current research focuses on the design of nanomaterials based on metal nanoparticles and metal–organic frameworks.

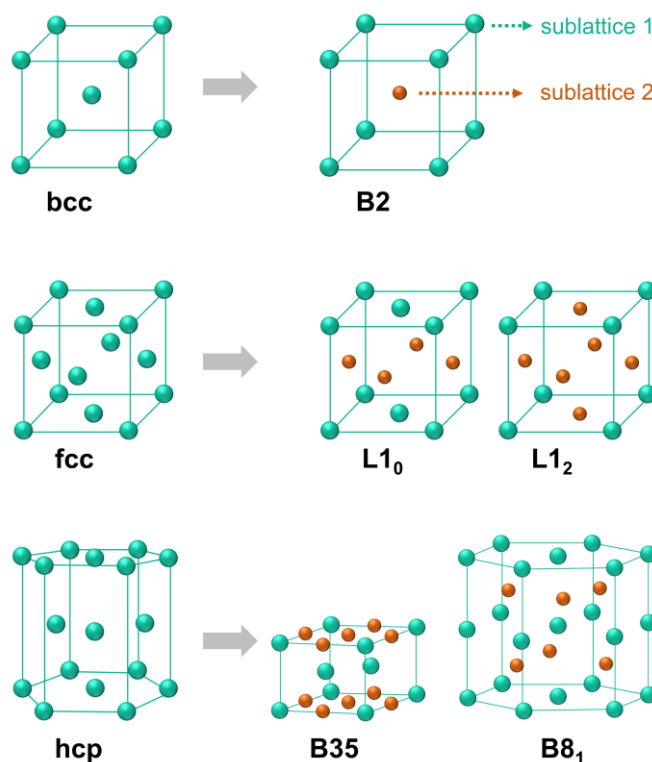
scarcity and high cost of PGMs have prompted efforts to develop alternative materials with improved catalytic performance and lower costs. Nanosizing and alloying are two important strategies for this purpose.^[13] Nanoparticles (NPs) exhibit high surface-to-volume ratios and quantum size effects, enabling precise control over their catalytic properties by modulating size, morphology, and surface modifications.^[14] Alloying with different metals allows for the fine-tuning of the electronic structure of elements, thereby improving both catalytic activity and stability.^[15] In addition, alloying with non-noble metals maintains the high catalytic activity of noble metals and reduces noble metal consumption. To date, noble metal-based and noble metal-free alloy NPs, ranging from binary to multi-element alloy NPs, have been extensively studied.^[16–18] Among them, high-entropy alloys (HEAs) containing five or more major elements in approximately equal atomic ratios have attracted significant attention as efficient electrocatalysts.^[19, 20] HEAs exhibit advantages such as the “cocktail effect”^[21], which refers to the unique properties arising from the complex interactions and synergistic effects of multiple elements, resulting in enhanced stability, strength, and performance of the alloy. Over the last decade or so, research on HEAs has mainly focused on simple solid-solution phases in which multiple elements randomly occupy the same lattice site.^[22–24]

Compared with solid-solution alloys, intermetallics are a unique class of alloys with well-defined atomic positions and ordered crystal structures.^[25,26] Solid-solution HEAs typically form simple crystal structures, namely face-centred cubic (fcc), body-centred cubic (bcc) and hexagonal close-packed (hcp) structures.^[27] The crystal structures of intermetallic compounds are usually derivatives of these primary crystal structures (Fig. 1). The ordered derivatives of the fcc-based crystal structure mainly include the L1₂, L1₀ and DO₂₂ structures, of which L1₂ and L1₀ are the most common crystal structures of noble metal-based intermetallic NPs.^[28–30] The most common

intermetallic structure derived from the bcc crystal structure is the B2 structure. Typical hcp-based intermetallic structures include the B8₁ and B35 structures. The simplest binary intermetallic compound consists of two elements in precise stoichiometric ratios, represented as A_xB_y, where each element occupies a specific atomic position in the crystal lattice. These specific positions, defined by the regular arrangement of atoms, are referred to as lattice positions or sublattices. Building upon this concept, the concept of high-entropy intermetallics (HEIs) was later proposed.^[25] HEIs retain the parent crystal structure of binary intermetallics (A_xB_y), but elements A and/or B substituted with multiple additional elements. Unlike conventional binary intermetallic compounds, the elemental occupancy at each sublattice site of HEI is random, similar to that of solid-solution alloys. HEIs combine the advantages of HEAs and intermetallics. The specific arrangement of multiple metal atoms within the crystal lattice results in unique coordination environments in HEI alloys.^[31] For example, in contrast to conventional binary intermetallics, the incorporation of multiple metal constituents in HEIs dilutes the identical metal (M₁)-metal (M₁) coordination, some metal atoms become surrounded by different metal atoms, leading to the unique “site segregation” phenomenon in HEI.^[32] The site isolation is very important in catalytic reactions, as it may result in higher selectivity for certain reactants and affect the electronic band structure of HEI by modifying the local electronic environment, thereby increasing catalytic activity.^[33]

Solid-solution Alloys

Intermetallics



Hiroshi Kitagawa completed his PhD at Kyoto University in 1991 whereafter he worked as Assistant Professor at Institute for Molecular Science (IMS) and Japan Advanced Institute of Science and Technology (JAIST). In 2000, he was appointed as Associate Professor at University of Tsukuba. He was appointed Professor of Chemistry at Kyushu University in 2003 and Professor at Kyoto University in 2009. He is currently Director of the network-type research institution Exploring Innovative Materials in Unknown Search Space, CREST. He has published more than 530 original research papers dealing with solid-state chemistry, coordination chemistry, nanoscience, low-dimensional electron systems, and molecular-based conductors.

Fig. 1 Typical crystal structures of solid-solution alloys and intermetallics.

Reports on HEIs began in 2016 and initially focused on bulk materials rather than NPs.^[25,34] This is because the synthesis of HEIs at the nanoscale is still challenging. The formation of intermetallic structures usually requires harsh annealing conditions, which inevitably lead to particle growth/aggregation or phase separation.^[35] In 2022, Cui et al.^[36] successfully synthesised for the first time (Pt_{0.8}Pd_{0.1}Au_{0.1})(Fe_{0.6}Co_{0.1}Ni_{0.1}Cu_{0.1}Sn_{0.1}) HEIs with an L1₀ structure, containing up to eight different elements and achieving particle sizes ranging from 4 to 5 nm. However, research on HEI NPs is still in its early stages. A literature review shows only approximately 28 publications on HEI NPs to date, many of which highlight their excellent activity in electrochemical catalysis.

Several review articles on HEIs have been published so far^[37–42], but most of them mainly focused on bulk materials, providing limited coverage of the synthesis strategies and catalytic applications of HEI NPs. Recently, two review articles have mentioned the catalytic applications of HEI NPs.^[35, 42] Building on recent progress, this review provide a more comprehensive overview of HEI nanomaterials, highlighting the various synthesis methods and their applications in electrocatalytic reactions.

2. The concept of entropy in HEI

The concept of HEA was first introduced in 2004.^[43, 44] The concentration of each element in a solid-solution HEA with a stable structure should be within the range of 5 – 35 at.%. The stability of the phase in solid-solution alloys can be explained thermodynamically by the change in Gibbs free energy (ΔG_{mix}):^[45–47]

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

where ΔH_{mix} and ΔS_{mix} represent the enthalpy and entropy of the mixture, respectively, and T is the temperature. A negative ΔG_{mix} is required for phase stability, and the enthalpy ΔH_{mix} accounts for interactions between the constituent elements, the entropy term $T\Delta S_{mix}$ reflects the contribution of configurational disorder. In HEA, the configurational entropy ΔS_{mix} plays a crucial role in stabilising the solid-solution phase, particularly at elevated temperatures, as the entropy term $T\Delta S_{mix}$ increasingly offsets unfavourable enthalpic contributions.

The configurational entropy is related to the number and proportion of constituent elements in the HEA at a constant temperature. The ideal configurational entropy ΔS_{mix} of a solid-solution alloy consisting of N elements can be expressed using the following equation:^[47,48]

$$\Delta S_{mix} = -R \sum_{i=1}^N x_i \ln x_i$$

where R is the ideal gas constant, valued at 8.31 J/(K·mol), N represents the number of elements, and x_i represents the atomic fraction of the i th element.

For intermetallic compounds, the crystal structure is ordered, meaning that the arrangement of atoms is not random and certain atoms are restricted to specific positions known as sublattices. For example, the indium–PGM (In–PGM) HEI NPs synthesised by Nakamura et al.^[49] possessed a B2 structure, in which the PGM atoms occupied the (1/2, 1/2, 1/2) positions, whereas the In atoms occupied the (0, 0, 0) positions. Therefore, the configurational entropy of different sublattices needs to be considered separately in intermetallic compounds.^[50–53] By summing the contribution of the entropy for each individual sublattice, the total configuration entropy of the intermetallics can be calculated using the following equation:

$$\Delta S_{mix} = -R \frac{\sum_s \sum_i a^s x_i \ln x_i}{\sum_s a^s}$$

where a^s is the number of sites on the s sublattice, and x_i represents the atomic percentage of the i th element on the s sublattice.

The configurational entropy ΔS_{mix} has been utilised to classify materials into categories such as high entropy, medium entropy and low entropy.^[54–56] However, Diplo et al.^[57] pointed out that configurational entropy is not applicable to all materials, such as ceramic materials. To address this limitation, they proposed a new entropy metric (EM) applicable to all materials, denoted by the following equation:

$$EM = \frac{\Delta S_{mix}}{R} \times L$$

where ΔS_{mix} is the calculated configurational entropy, and L represent the total number of sublattices. Typically, if the value of EM is ≥ 1.5 , the material is classified as high entropy material, when $1 \leq EM < 1.5$, the material is regarded as medium entropy, and when EM is < 1 , the material is regarded as low entropy. **Table 1** lists some examples of the calculated EM values for reported multi-element intermetallic alloy NPs.

Table 1. Examples of calculated EM values for multi-element intermetallic alloys ($L=2$)

Materials	$\Delta S_{mix}/R$	EM	EM Classification	Ref.
(Pt _{0.8} Pd _{0.1} Au _{0.1})(Fe _{0.6} Co _{0.1} Ni _{0.1} Cu _{0.1} Sn _{0.1})	0.93	1.87	high entropy	36
Pt ₄₅ Fe ₁₅ Co ₁₃ Ni ₁₂ Cu ₁₅	0.76	1.52	high entropy	58
Pt _{36.8} Ir _{12.6} Fe _{20.0} Co _{18.9} Cu _{11.7}	0.82	1.65	high entropy	59
In(IrRhRuPdPt)	0.78	1.56	high entropy	49
Pt _{29.5} (CuPdAgFe) _{70.5}	0.88	1.75	high entropy	60

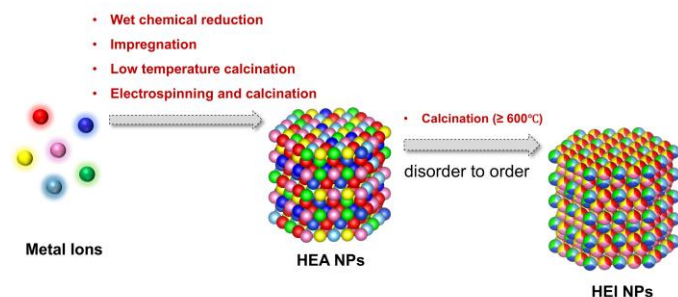
Pt ₄ FeCoCuNi	0.78	1.56	high entropy	61
Sb _{45.7} (FeCoNi)	0.60	1.19	medium entropy	62
Sb ₅₀ (FeCoCuNi)	0.69	1.39	medium entropy	62
Sb ₅₀ (FeCoCuNiZn)	0.80	1.61	high entropy	62
(Ti _{0.25} V _{0.25} Nb _{0.25} Ta _{0.25})C	0.69	1.39	medium entropy	63

3. The synthesis methods of HEI NPs

Since 2021, researchers have explored various methods for synthesising HEI NPs, which can be classified into two main categories (Fig. 2).

The first method is a two-step process, where HEA NPs are first synthesised, followed by a calcination step to induce the final formation of HEI NPs. Examples of these methods include wet chemical reduction followed by calcination, impregnation-reduction method, electrospinning and calcination method as well as calcination of metal precursors. In the wet chemical reduction and calcination method, metal precursors are chemically reduced to form HEA NPs, which are subsequently subjected to calcination. Similarly, the impregnation-reduction method involves depositing metal precursors onto a support, followed by calcination under a reducing condition to produce HEI NPs. In the electrospinning and calcination method, metal precursors are usually first electrospun to obtain nanofibres and then annealed to obtain HEI NPs. The metal precursor calcination method typically requires two annealing steps: the first to form HEA NPs and the second to induce a disorder-to-order transition, resulting in HEI NPs.

Two-step method



One-step method

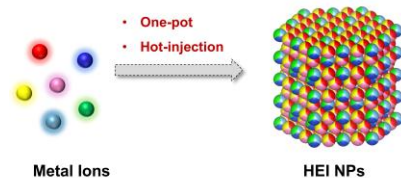


Fig. 2 The category of synthesis methods for HEI NPs.

The second method is a one-step process, which directly synthesises HEI NPs in a single reaction, such as one-pot method and hot-injection method. Details of these approaches are described in the following sections.

3.1 Two-step process

3.1.1 Wet chemical reduction and calcination method

Wet chemical reduction and calcination method typically consists of two steps: reduction and calcination. Wet chemical reduction is a widely used approach for the synthesis of NPs. In this process, metal precursors are typically reduced to form disordered HEA NPs. Commonly used reducing agents include oleylamine (OAm) and triethylene glycol (TEG). For metal ions with high reduction potentials, stronger reducing agents such as sodium borohydride (NaBH₄) can also be employed to facilitate the reduction process. Following the reduction step, a disorder-to-order transition is achieved through the calcination of the pre-obtained HEA NPs in a reducing gas atmosphere, typically at temperatures exceeding 600 °C. A high temperature induces atomic rearrangement and contributes to overcoming the energy barrier for the disorder-to-order transformation, resulting in the formation of ordered HEI NPs.

Nakamura et al.^[49] synthesised In-PGM HEI NPs in 2023 using a wet chemical reduction and calcination method. First, precursor NPs (PNPs) were prepared by hot injection of metal precursors and NaBH₄ into TEG. Then, the PNPs were loaded onto carbon (VXC72R, Cabot Corp., USA) and annealed at a mild condition of 350 °C for 20 min under H₂ atmosphere (101 kPa) and rapidly cooled to room temperature with an ice-water bath to obtain In-PGM HEI NPs/C. Synchrotron in-situ powder X-ray diffraction (PXRD) indicated that PNP transformed from a disordered solid-solution structure to In-PGM HEI NPs with a B2 structure at temperatures above 300 °C (Figs. 3a and b). Atomic resolution high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) images showed that In and PGM atoms occupied different sublattices in the B2 structure (Figs. 3c–j). The energy dispersive X-ray (EDX) results indicated that the molar ratio of indium to PGM was 1:1 (Fig. 3k). In this synthesis, the transition temperature was below 600 °C, which may be due to the addition of low melting point metals. Liang et al.^[64] also demonstrated that the introduction of low-melting-point metals (M' = Sn, Ga, In) allowed for the disorder-to-order transition temperature of PtM (M = Fe, Co, Ni, etc.) alloy NPs to be lower than 450 °C.

During the calcination process to obtain an ordered arrangement, sintering or morphological changes of the NPs may occur if the annealing temperature is very high.^[65,66] This issue can be improved by the provision of support.^[67] A porous support or an external structure (template) can be adapted to spatially confine the NPs and maintain the nanoscale size during the heating process. Additionally, the template can provide a predetermined framework for the size, shape, and structure of the HEI NPs so that the obtained NPs are usually of a specific shape and uniform in size.

Feng et al.^[59] obtained 6 nm PtIrFeCoCu HEI (PIFCC-HEI) NPs with an ordered L1₀-FePt structure (Fig. 3l) by simple chemical co-reduction followed by an annealing process. First, NaBH₄ was injected as a reducing agent into a solution containing the metal precursor and carbon (Ketjen-black, EC-300J, Lion Specialty Chemicals Co. Ltd (Japan)) to obtain the intermediate NPs,

followed by annealing the intermediate NPs at 850 °C for 4 h under a H₂/Ar atmosphere. Carbon supports were pre-added to the reaction solution with metal precursors, which allowed the NPs to grow in-situ and bind tightly to the carbon supports, preventing their agglomeration during annealing. The EDX line scans (Fig. 3m) revealed a uniform distribution of all metal

elements and a molar ratio of Pt/Ir/Fe/Co/Cu of 34.8:12.3:21.7:20.0:11.2 for a single PIFCC-HEI NP. Aberration-corrected HAADF-STEM images revealed the ordered structure of the PIFCC-HEI NPs, with “Z-contrast” brightness allowing sublattices to be distinguished owing to the atomic number difference between Pt/Ir and Fe/Co/Cu atoms (Figs. 3n and o).

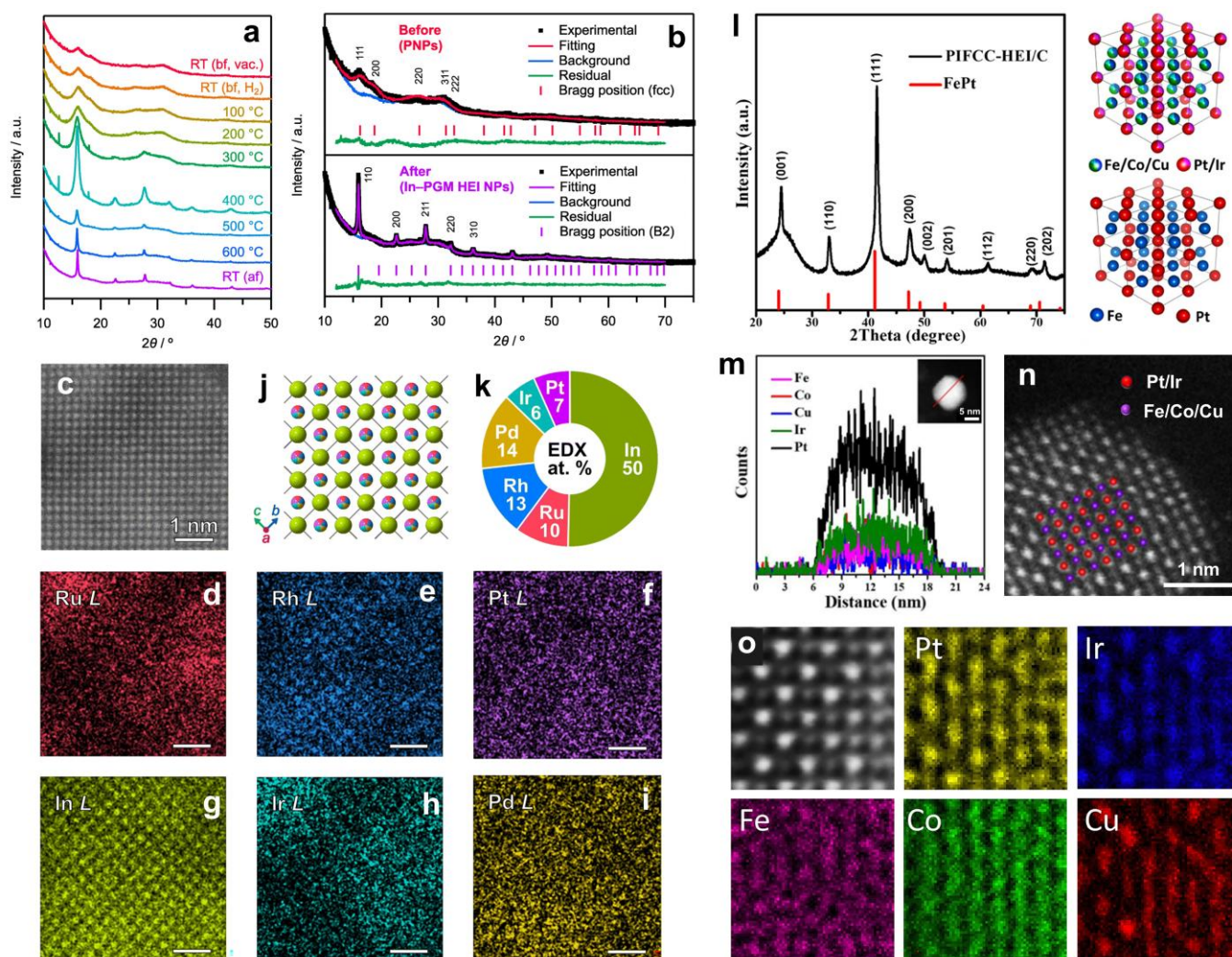


Fig. 3 (a) In-situ Synchrotron PXRD of In-PGM NPs/C. (b) Rietveld refinement of synchrotron PXRD of In-PGM NPs before and after heating (wavelength: 0.630407(1) Å). (c–i) Atomic-resolution HAADF-STEM image and corresponding elemental mappings of In-PGM HEI NPs/C. (j) The model of In-PGM NPs from the same perspective as (c). (k) EDX analysis of the region in (a). Reprinted with permission from ref. 49. Copyright 2023 The Royal Society of Chemistry. (l) PXRD of PIFCC HEI NPs (Cu K α). The Insets show the crystal structures of PIFCC HEI and PtFe. (m) EDX line scan profiles of a PIFCC HEI NP. (n) Atomic-resolution HAADF-STEM image of a PIFCC HEI NP. (o) Atomic-resolution HAADF-STEM image and corresponding elemental mappings of PIFCC HEI NPs. Reprinted with permission from ref. 59. Copyright 2023 American Chemical Society.

Wang et al. [68] synthesised a series of mesoporous Pt-based HEI NPs with multiple elemental constituents through a template strategy (Fig. 4a). In a typical synthesis, rigid cubic *la3d* silica (KIT-6) [69] was used as a hard template. First, chemical co-reduction of noble metal precursors (PtCl₄²⁻, PdCl₄²⁻, and/or Rh³⁺) within the KIT-6 template yielded M-PtM₁ NPs/KIT-6 (M₁ = Pd and/or Rh). Subsequently, transition metal salts (M₂ = Fe or Zn) were physically mixed with M-PtM₁/KIT-6 and annealed for 6 h at a high temperature (>480 °C) under H₂/N₂ (5:95) atmosphere, forming ternary mesoporous intermetallic (M-PtM₁Fe and M-PtM₁Zn). Subsequently, transition metal salts M₃ (M₃ = Co, Ni,

Mn, and/or Ga) were introduced under the same conditions to prepare ordered MHEI/KIT-6. Finally, the KIT-6 template was removed by etching with dilute 5% HF to obtain MHEI NPs. Using this process, a series of quinary (PtPdFeCoZn, PtRhFeCoNi, PtPdFeCoGa, PtPdZnCoNi, and PtPdZnCoGa), senary (PtPdRhFeCoNi), septenary (PtPdRhFeCoNiGa), and octonary (PtPdRhFeCoNiGaMn) MHEI NPs with L1₀ PtFe- or PtZn-like crystal structures were successfully synthesised (Fig. 4b). The obtained HEI NPs exhibited polyhedral morphology, were highly uniform in distribution, and had particle sizes ranging from 160 to 200 nm.

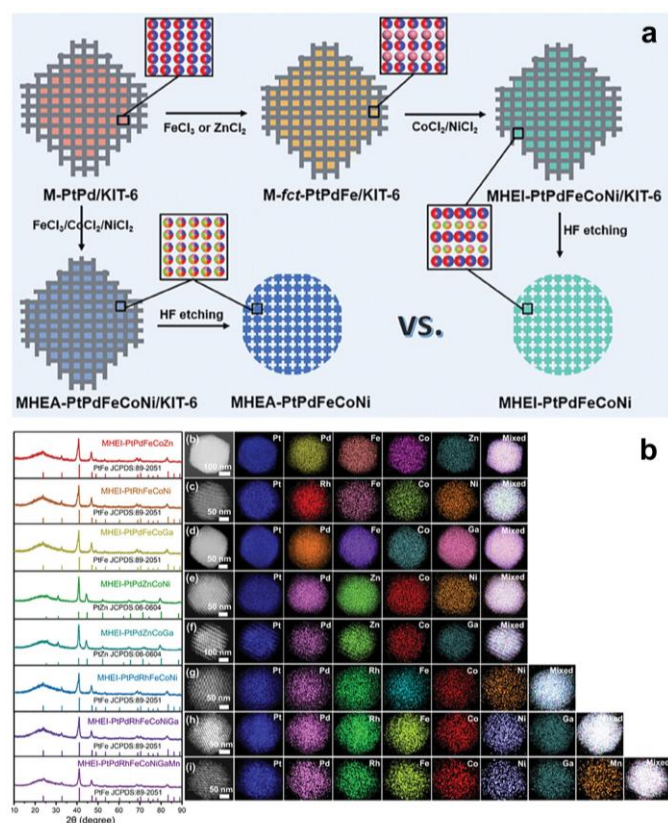


Fig. 4 (a) Synthesis process for MHEI- and MHEA-PtPdFeCoNi NPs. (b) PXRD patterns ($\text{Cu K}\alpha$) and STEM EDX mapping images of quinary (PtPdFeCoZn, PtRhFeCoNi, PtPdFeCoGa, PtPdZnCoNi and PtPdZnCoGa), senary (PtPdRhFeCoNi), septenary (PtPdRhFeCoNiGa), and octonary (PtPdRhFeCoNiGaMn) MHEI NPs. Reprinted with permission from ref. 68. Copyright 2024 Wiley-VCH.

3.1.2 Impregnation-reduction method

The impregnation-reduction method is another widely used approach for the synthesis of NPs, particularly for supported catalysts. This process involves the physical mixing of metal precursors with a porous support material, such as Vulcan XC-72 carbon, silica, and Zn-based dodecahedral porous carbon nitride (Zn-DPCN), by impregnation. The supported metal precursor was then annealed in a reducing atmosphere, such as H_2 , to facilitate metal ion reduction and HEI NPs formation. Under appropriate conditions, annealing can promote the

atomic ordering necessary for the formation of HEIs. This method is advantageous for its simplicity and versatility with various precursors and supports. **Table 2** gives a summary of the reported HEI NPs synthesised by the impregnation-reduction method.

In 2022, for the first time, Ma et al. [70] prepared NiFeCuGaGe HEI NPs with SiO_2 as support using the impregnation-reduction method. Firstly, the metal salts were thoroughly mixed with SiO_2 via impregnation and then calcined in a flowing H_2 (40 mL min^{-1}) at 400°C for 1 h, finally calcined again at 700°C to obtain the HEI NPs (ramping rate of $10^\circ\text{C min}^{-1}$). The synthesised NiFeCuGaGe HEI NPs had an average particle size of 4.9 nm, and the XRD results indicated that the NPs had a B2 NiGa intermetallic structure (CsCl-type).

Chen et al. [71] synthesised PtFeCoNiCuZn (PFCNCZ) HEI NPs with a particle size of 2 nm, which is one of the smallest reported HEI NPs. First, metal salts of Pt, Fe, Co, Ni, and Cu were dispersed onto the porous carbon nitride Zn-DPCN by impregnation, and the mixtures were then treated with flowing H_2/Ar gas at 800°C for 4 h to form the HEI NPs. The PFCNCZ-HEI NPs are confined to the mesoporous structure of the Zn-DPCN support, which effectively inhibits the agglomeration of the NPs. Additionally, through the interaction between the N atoms of Zn-DPCN and HEI NPs, the migration of the NPs was also inhibited.

Wang et al. [72] synthesised multiwalled carbon nanotube (MWCNT)-supported PtRhFeNiCu HEI NPs using an impregnation-reduction method. In a typical synthesis, firstly, the metal precursor was physically mixed with the MWCNT by impregnation and then calcined under a 10% H_2/Ar atmosphere at 400°C for 2 h to obtain the HEA NPs/C. Finally, the HEA NPs/C were annealed under 10% H_2/Ar at 700°C for 2 h to obtain PtRhFeNiCu HEI NPs/C. In the impregnation reduction method, the annealing process sometimes involves two steps. [33, 70, 72–75] The first step involves heating at a relatively low temperature ($<600^\circ\text{C}$), typically providing disordered solid-solution HEA NPs. The second step involves annealing at a high temperature ($>600^\circ\text{C}$), where a disorder-to-order transition occurs, resulting in the formation of the HEI NPs.

As mentioned above, the selection of a suitable support, such as a porous material, is essential for the impregnation-reduction process. In addition, the support surface can be modified to anchor the NPs using specific functional groups. This improves the dispersion and helps maintain the structure and morphology of the NPs during the subsequent annealing process.

Table 2. Summary of HEI NPs synthesised by impregnation reduction method

Element	Support	Temp. ($^\circ\text{C}$)		Gas		Structure	Size (nm)	Ref.
		Step 1	Step 2	Step 1	Step 2			
NiFeCuGaGe	SiO_2	400	700	H_2		B2	4.90	70
PtRhFeNiCu	MWCNT	400	700	10% H_2/Ar	10% H_2/Ar	B2	-	72
$\text{Pt}(\text{FeCoNiCuZn})_3$	Vulcan XC-72 carbon	150	700	10% H_2/Ar	10% H_2/Ar	L1_2	5.75	73
$(\text{PtPdIrRu})_2\text{FeCu}$	Vulcan XC-72 carbon	200	500	10% H_2/Ar	10% H_2/Ar	L1_0	1.80	74
$(\text{PtCoNi})(\text{SnInGa})$	CeO_2	500	600	Air	H_2	B8_1	4.00	75

(PtCoCu)(GeGaSn)	Ca-SiO ₂	400	700	Air	H ₂	B14	2.20	33
PtFeCoNiCuZn	Zn-DPCN	800	-	H ₂ /Ar	-	L1 ₀	2.00	71
PtFeCoNiMn	polystyrene (PS) nanospheres	1000	-	5% H ₂ /N ₂	-	L1 ₀	4.90	76
CoFeNiCuPd	nitrogen-rich mesoporous carbon	750	-	NH ₃	-	L1 ₂	-	77
Pt ₄ FeCoCuNi	sulphur-doped carbon supports	1000	-	10% H ₂ /Ar	-	L1 ₀	5.10	61
Pt ₄ FeCoNiCu Pt ₅ FeCoNiCuMn	sulphur-doped carbon supports	1100	-	5% H ₂ /Ar	-	L1 ₀	<5.00	78

Wang et al. [61] synthesised Pt-based intermetallic NPs via a sulphur-anchored strategy (Fig. 5a). First, sulphur-doped carbon (SC) supports were synthesised through the carbonylation of 2,2'-bithiophene. After that, a mixture of metal salts was loaded onto the SC support by wet-impregnation method. Finally, the SC-loaded Pt₄FeCoCuNi NPs were formed by annealing in flowing Ar/H₂ gas at a flow rate of 115/15 standard cubic centimetres per minute. The NPs with different degrees of order can be obtained by varying the annealing temperature and time, namely 1000 and 700 °C for 2 h for the highly ordered and partially ordered sample, respectively, and 500 °C for 25 min for the disordered sample. The degrees of order were 92%, 65%, and 0 for the highly ordered, partially ordered, and disordered Pt₄FeCoCuNi NPs, respectively. The

disordered, partially ordered, and highly ordered NPs had average particle sizes of 3.6, 4.5 and 5.1 nm, respectively, with narrow size distributions. The crystal structure of the highly ordered Pt₄FeCoCuNi NPs matched to L1₀ PtCo phase. Yang et al. [78] prepared quinary Pt₄FeCoNiCu and senary Pt₅FeCoNiCuMn intermetallic NPs on SC supports by sulphur-anchored synthesis. The prepared intermetallic HEI NPs, with particle sizes below 5 nm, exhibited an ordered L1₀ structure of space group P4/mmm. The abundant S sites in the SC support, with strong interactions with the Pt atoms, can increase the adhesion energy of the NPs on the SC supports and slow down the migration and/or agglomeration of the NPs to inhibit their sintering.

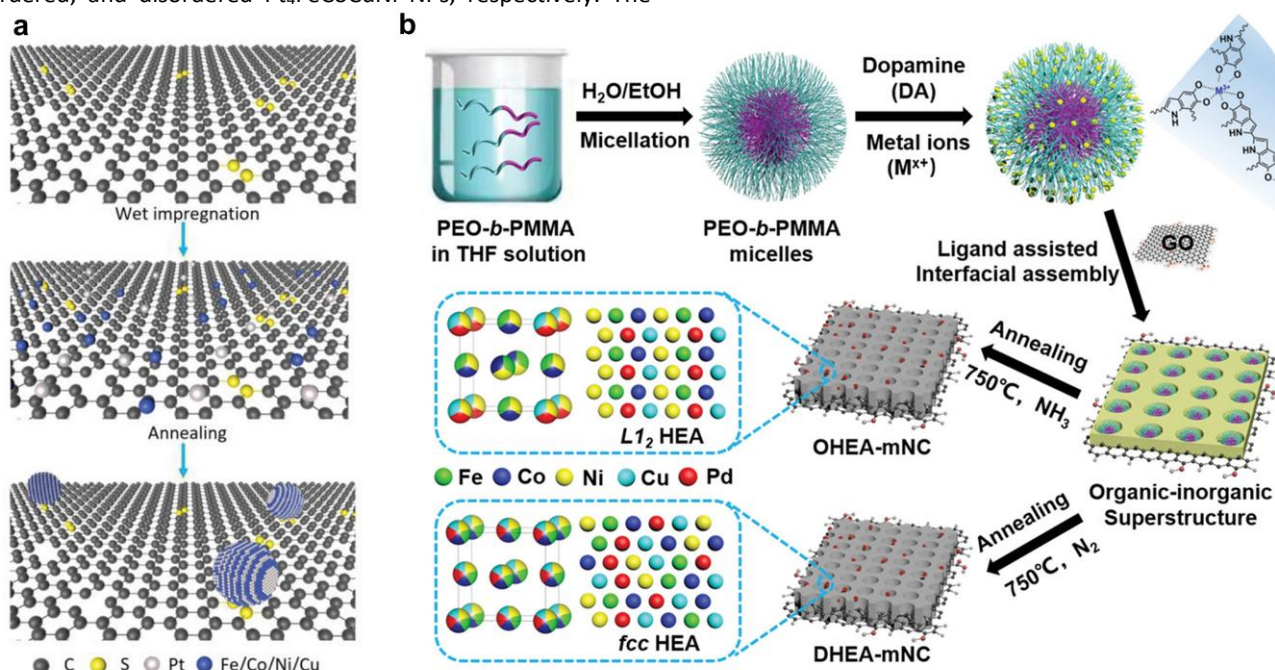


Fig. 5 (a) Synthesis strategy for Pt₄FeCoCuNi NPs with different degrees of ordering. Reprinted with permission from ref. 58. Copyright 2023 Wiley-VCH. (b) Synthesis Process for CoFeNiCuPd NPs with different crystal structures. Reprinted with permission from ref. 77. Copyright 2022 Wiley-VCH.

Zhu et al. [77] adopted a ligand-assisted strategy to obtain CoFeNiCuPd NPs (Fig. 5b). In a typical synthesis, dopamine (DP), metal precursors, and graphene oxide were sequentially added to a poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO-*b*-PMMA) diblock copolymer solution. The DP used in the reaction was rich in catechol and amine groups, which can efficiently interact with most metals and substances. The mixtures were

then annealed at 750 °C under different gas atmospheres. Under an N₂ atmosphere, CoFeNiCuPd HEA NPs with fcc structure were obtained (DHEA NPs), whereas under an NH₃ atmosphere, CoFeNiCuPd HEA NPs with an ordered L1₂ structure were formed (OHEA NPs). The formation of two different structures in the NH₃ and N₂ atmospheres can be attributed to the stabilising effect of the respective gas molecules. Density functional theory (DFT) calculations

indicated that the adsorption energy of NH_3 on OHEA-mNC (-0.3197 eV) is larger than that of N_2 (-0.1139), which indicates that the adsorption of NH_3 on OHEA-mNC is more stable. While on DHEA-mNC, the adsorption energy of N_2 was more negative (-0.4444 eV), indicating that N_2 was more strongly bound on DHEA-mNC. Additionally, the alkalinity of NH_3 leads to partial etching of the mesoporous carbon skeleton during high-temperature treatment, exposing the HEA NPs directly to NH_3 molecules. This process facilitates the rearrangement of metal atoms, promoting the formation of stable ordered structures under an NH_3 atmosphere.

In another study, Zhu et al. [79] used the same ligand-assisted strategy again to obtain a series of quinary $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}$, $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}$, $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}$ and septenary ($\text{Pt}_{0.8}\text{Pd}_{0.2}$) ($\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Mn}_{0.2}$) HEI NPs with an L_{10} structure. By utilizing a two-step annealing process in an NH_3 atmosphere—initially at 750 °C for 120 min, followed by an additional 120 min at 650 °C—an impressive 93.8% ordering of the $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}$ HEI NPs was achieved (Figs. 6a and b). In comparison, annealing in an N_2 atmosphere can also induce a certain degree of chemical ordering in HEI NPs (58.5%), but it generally necessitates a higher temperature (950 °C) and an extended duration (300 min). Therefore, it can be noted that in addition to the annealing temperature, the gas atmosphere also affects the crystal structure and the order degree of the NPs.

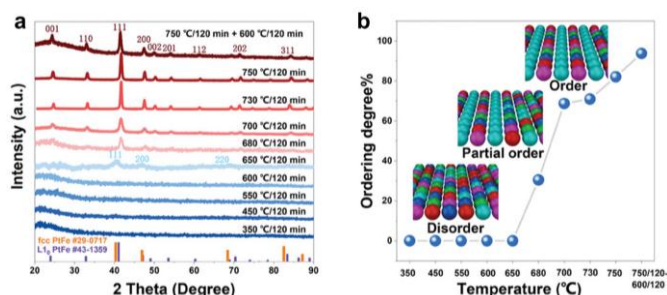


Fig. 6 (a) XRD patterns of $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}$ after annealing at different temperatures (Cu K radiation). (b) Temperature-dependent ordering degree of thermally treated samples. Reprinted with permission from ref. 79. Copyright 2025 Wiley-VCH.

3.1.3 Electrospinning and calcination method

Recently, the electrospinning and annealing methods were also used for the synthesis of HEI NPs. Hao et al. [80] obtained (PtIr)(FeMoBi) HEI NPs via a combination of electrospinning and high-temperature annealing. Initially, metal salts of Fe, Mo, Bi, Pt, and Ir and polyacrylonitrile (PAN) were dissolved in N, N-dimethylformamide to form a homogeneous solution, which was then electrospun using a YFSP-T electrospinning machine to obtain the nanofibers. The obtained nanofibers underwent pre-oxidation at 230 °C in air, followed by graphitization at 1000 °C for 3 h under an Ar atmosphere, forming (PtIr)(FeMoBi) HEI NPs supported on carbon nanofibers (CNFs). The PtIrFeMoBi HEA NPs was achieved by modifying the graphitization conditions, reducing the temperature to 800 °C and shortening the duration to 0.5 h. The structural characterization revealed that the synthesised (PtIr)(FeMoBi) HEI NPs exhibited the ordered L_{10} structure with an average diameter of about 3.95 ± 1.38 nm (Figs. 7a–c). Liu et al. [81] used the same electrospinning and calcination (initial stabilization at 230 °C in air, followed by

1000 °C for 3 h under an Ar atmosphere) method to successfully synthesise (FeCoNi)(RuPt) HEI NPs. The (FeCoNi)(RuPt) HEI NPs have an average size of approximately 20 nm with an L_{10} -type CoPt intermetallic structure (Figs. 7d–f).

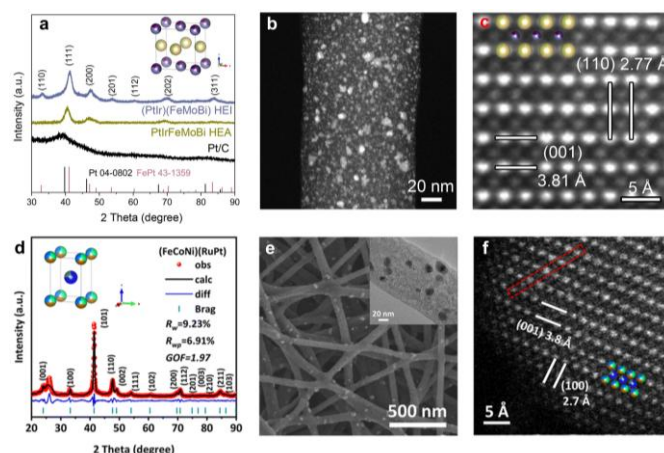


Fig. 7 (a) XRD patterns comparing different materials. The inset illustrates the corresponding unit cell of (PtIr)(FeMoBi)/CNFs (Cu K α). (b) HAADF-STEM image of the (PtIr)(FeMoBi) HEI NPs. (c) Atomic resolution HAADF-STEM image of a typical (PtIr)(FeMoBi) NP. Reprinted with permission from ref. 80. Copyright 2025 Wiley-VCH. (d) XRD pattern of (FeCoNi)(RuPt) HEI NPs (Cu K α). The inset illustrates the corresponding unit cell of (FeCoNi)(RuPt) HEI NPs. (e) SEM image and the inset is the corresponding TEM image of (FeCoNi)(RuPt)/CNFs. (f) Atomic resolution HAADF-STEM image of an (FeCoNi)(RuPt) HEI NP. Reprinted with permission from ref. 81. Copyright 2025 The Royal Society of Chemistry.

In electrospinning method, PAN is typically utilised due to its excellent spinnability, which allows for the formation of continuous and uniform nanofibers to support the metal precursors during the electrospinning process. During the subsequent thermal treatment (carbonization), PAN is converted into conductive CNFs, which serve as a highly dispersed, conductive and robust support for the HEI NPs. Moreover, the presence of PAN fibers helps to confine the growth of metal species during annealing, effectively preventing aggregation and promoting the formation of uniformly distributed HEI NPs with small sizes.

3.1.4 Calcination of the metal precursor

In the impregnation-reduction method, metal precursors are typically loaded onto a support and then heat-treated. However, in 2022, Soltani et al. [62] obtained Sb-based intermetallic NPs, SbNiCoFeCuZn , by the direct calcination of the metal precursor without a support. In a typical synthesis, the metal chloride salt was dissolved in an ethanol solvent containing polyvinylpyrrolidone (PVP). After drying, the mixture underwent two-step calcination. The first step involved calcinating the precursor at 600 °C for 2 h in the air to decompose the PVP polymer and induce crystallisation, resulting in the formation of metal oxide NPs. In the second step, calcination was conducted in a H_2 atmosphere (without flow) at 500–510 °C for 2–2.5 h to remove oxygen and form HEI NPs. PVP was thermally decomposed approximately at 480 °C, so the temperature of calcination in the first step should exceed 500 °C. During the decomposition of PVP, gases such as NO, CO, CO_2

and water vapour are released, effectively preventing the aggregation of NPs. The obtained SbNiCoFeCuZn NPs had a particle size ranging from 31.6 to 42.5 nm, with a main structure of B8 NiAs-type. In 2023, Soltani et al.^[82] succeeded in synthesising intermetallic (NiCoFeCu)_{1-x}Sb_x NPs with a NiAs-type structure using the same precursor calcination method.

In addition to conventional thermal annealing, HEI NPs can also be obtained using Joule heating of metal precursors. In this method, an electric current is applied to generate localised heat, allowing precise control of the reaction temperature. Cui et al.^[36] achieved a phase transition of NPs from disordered to ordered crystal structures by Joule heating and synthesised multi-principal element (up to eight elements) intermetallics (MPEIs) with ultra-small (4–5 nm) particle sizes. Taking the synthesis of (Pt_{0.8}Pd_{0.1}Au_{0.1})(Fe_{0.6}Co_{0.1}Ni_{0.1}Cu_{0.1}Sn_{0.1}) MPEI NPs as an example, metal precursors (H₂PtCl₆, PdCl₂, HAuCl₄, FeCl₃, CoCl₂, NiCl₂, CuCl₂, and SnCl₂) were first subjected to rapid Joule heating at approximately 1100 K for 55 ms on a carbon substrate to form disordered solid-solution HEA NPs. The obtained HEA NPs were then reheated at approximately 1100 K for 5 min via Joule heating to promote the rearrangement of atoms into thermodynamically more stable ordered intermetallic NPs. The heating process was performed in an Ar-filled glove box. This was followed by rapid cooling to preserve the final ordered structure and obtain (Pt_{0.8}Pd_{0.1}Au_{0.1})(Fe_{0.6}Co_{0.1}Ni_{0.1}Cu_{0.1}Sn_{0.1}) MPEI NPs. Compared with the conventional annealing method, the Joule heating method requires a shorter heating time, thus, the obtained particles tend to be in a single-crystalline phase with a small and uniform particle size.

3.2 One-step process

The synthesis methods mentioned above usually involve two steps, such as reduction followed by heat treatment, and are relatively complicated. The methods for obtaining HEI NPs by one-step reduction at high temperatures are increasingly attractive, such as one-pot synthesis and hot injection. In these methods, calcination at high temperatures is not required, allowing HEI NPs to be obtained under relatively mild conditions at lower temperatures (usually below 350 °C). The details of these methods are as follows.

3.2.1 One-pot method

The one-pot method has been commonly used to synthesise intermetallic NPs such as intermetallic hexagonal PtSnBi nanoplates,^[83] Pd₃Pb square nanoplates,^[84] and intermetallic hcp-PtBi/fcc-Pt core-shell nanoplates.^[85] In a typical synthesis, OAm and octadecene (ODE) are used as solvents and surfactants, ascorbic acid is used as a reducing agent, and the mixture is heated to obtain HEI NPs. The addition of other structure-directing agents, such as cetyltrimethylammonium bromide (CTAB) and NH₄Br facilitated the control of the shape of the NPs. Consequently, the synthesised NPs usually have specific morphologies, such as hexagonal or square plates.

Chen et al.^[86] reported the first synthesis of hexagonal PtRhBiSnSb HEI nanoplates (average edge length ≈ 6.2 nm) (Figs. 8a–c). To synthesise PtRhBiSnSb HEI nanoplates, 20.4 mg of Pt(acac)₃, 6.9 mg of Rh(acac)₃, 17.5 mg of Bi(act)₃, 3.0 mg of SnCl₂, 3.8 mg of SbCl₃, 80 mg of ascorbic acid, and 350 mg of CTAB were dissolved in a solution containing 5 mL each of ODE and OAm. The mixture was heated to 220 °C and kept at this temperature for 1 h. XRD analysis showed that the PtRhBiSnSb HEI nanoplates possess a structure analogous to binary hcp-PtBi

type intermetallic compounds (Fig. 8d). The HAADF-STEM images observed along different axes reveal an ordered arrangement of atoms in the HEI nanoplates (Figs. 8e–g). The authors assumed that the formation mechanism of HEI nanoplates begins with the initial formation of 2D Bi-complex templates, followed by the reduction of Pt and Sn species, the subsequent reduction of Rh and Sb species, the decomposition of Bi complexes, and finally, the diffusion and ordering of Pt, Rh, Bi, Sn and Sb atoms.

The one-pot method is an efficient and straightforward synthesis strategy that allows the sequential reduction, nucleation, structure control, and growth of metal precursors within a single reaction system, without complex multi-step procedures.

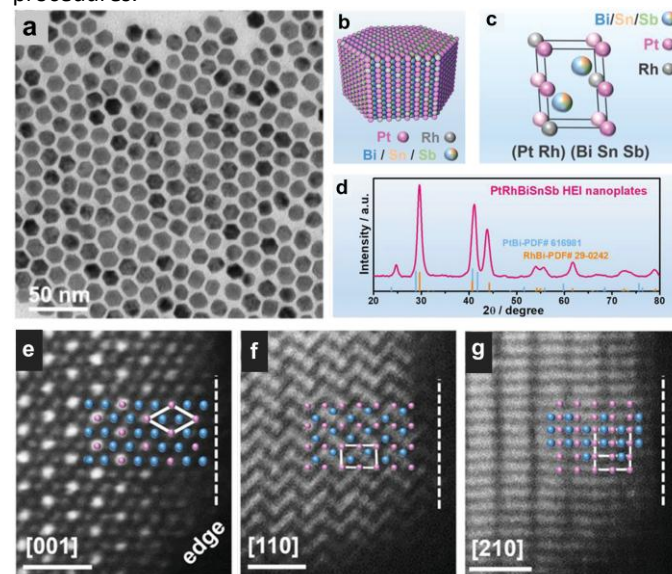


Fig. 8 (a) TEM image, (b) Schematic of the atomic arrangement, (c) Schematic of crystal units and (d) PXRD pattern of hexagonal PtRhBiSnSb HEI nanoplates (Cu K α), (e–g) HAADF-STEM images of HEI nanoplates observed along different axes. The blue and pink spheres represent Pt/Rh and Bi/Sn/Sb atoms, respectively. Scale bar: 1 nm. Reprinted with permission from ref. 86. Copyright 2022 Wiley-VCH.

3.2.2 Hot-injection method

The hot-injection method typically involves the rapid injection of a precursor solution into a preheated reaction medium, usually containing a solvent and surfactant, under inert atmospheric conditions. The rapid increase in temperature upon injection promoted the transient nucleation of nanocrystals, followed by the controlled growth of the nanocrystals. Soliman et al.^[87] synthesised (PdRhIrPt)Sn HEI NPs via the hot-injection method. In a typical synthesis process, a mixture of 6 mL of OAm and 10 mL of ODE was heated to 315 °C under Ar. Subsequently, a precursor solution containing SnCl₂, Pd(acac)₂, Rh(acac)₃, IrCl₄ and Pt(acac)₂ (4 mL in total) was gradually injected into the preheated solution (315 °C) at a controlled rate of 0.25 mL/min. After completion of the reaction, the reaction flask was cooled from 315 to 230 °C, followed by quenching in a water bath to obtain the HEI NPs. Slow injection promoted the formation of HEI NPs by regulating the rapid reduction of Pd and Pt salts. The obtained (PdRhIrPt)Sn HEI NPs exhibited a flower-like morphology and an hcp Ni₂In-type

structure. By investigating the form and growth pathways of the NPs, the formation of flower-like particles and their structure was closely related to the constituent elements and their proportions, providing insights into the morphological control of HEI NPs.

Thus far, we have reviewed various reported synthesis methods for HEI NPs. Although several approaches have been proposed, the synthesis of HEI NPs remains challenges. Most of the current synthesis methods for HEI NPs involve high-temperature calcination (above 600 °C), which might lead to particle aggregation. Therefore, the development of milder synthetic methods is expected to be the focus of future research. Additionally, based on the definition of entropy for an HEI, the EM of the HEI should exceed 1.5. However, some of the currently reported multi-element intermetallic NPs cannot satisfy this requirement (**Table 1**). Thus, among the HEI NPs presented in this review, some did not fully meet the criteria for HEI classification. Truly meeting the definition of HEI remains a challenge, as only a limited number of successful synthesis reports are available. Further advances in synthesis techniques are highly anticipated to address these challenges.

4. Electrochemical catalytic properties of HEI NPs

HEI NPs have been widely used in catalytic reactions, including in thermal catalysis, such as propane dehydrogenation [33] and acetylene semihydrogenation [70], as well as in electrocatalysis, and have demonstrated excellent catalytic properties. In this review, we focus on the applications of HEI NPs in electrocatalysis. Several publications have reported HEI NPs as electrochemical catalysts, focusing on (1) HER, (2) NO₃RR, (3) formic acid (HCOOH) oxidation reaction (FAOR), (4) alcohol oxidation reaction (AOR), and (5) ORR.

4.1 HER

H₂ is globally recognised as an ideal green energy source and an important chemical material.^[88] The HER is a critical half-reaction in water electrolysis, enabling large-scale and cost-effective H₂ production.^[89,90] However, several challenges hinder the widespread adoption of HER catalysts, including overdependence on precious metals, such as Pt and Ru^[91,92], slow reaction kinetics, and high overpotentials in alkaline conditions.^[93,94] These factors contribute to the high costs and limit the scalability of alkaline electrolysis for H₂ production.^[95,96] In addition, some Ru-based catalysts are relatively unstable and easily dissolve under acidic conditions.^[97] As a potential solution, HEI NPs have attracted attention owing to their catalytic

properties. The multi-metal constituents of HEI allow for a reduction in the usage of precious metals. Additionally, the multi-element nature of HEI NPs allows the electronic structure of the components to be tuned, thereby enhancing catalytic performance. The uniquely ordered geometric property of HEI NPs provides site isolation for the metal constituents and improves the stability of the NPs in the catalytic reaction.

Zheng et al.^[60] synthesised structurally ordered PtCuPdAgFe HEI NPs (PCPAF-HEI NPs) and investigated their HER electrochemical performance in a 0.5 M H₂SO₄ solution. In comparison with disordered PCPAF-HEA/C and commercial Pt/C, PCPAF-HEI/C exhibited a lower overpotential of 24 mV at a current density of 10 mA cm⁻² (**Fig. 9a**). The Tafel slope of PCPAF-HEI/C (29 mV dec⁻¹) was lower than that of PCPAF-HEA/C (38 mV dec⁻¹) and Pt/C (35 mV dec⁻¹), indicating faster HER kinetics (**Fig. 9b**). In addition, the long-term stability test was carried out in 0.5 M H₂SO₄ solution for 140 h at 100 mA cm⁻², with only a negligible change in voltage (**Fig. 9c**), demonstrating the excellent stability of PCPAF-HEI/C. According to the DFT calculations, the absolute hydrogen-adsorption free energies (ΔG_H) of the Pt site in PCPAF-HEI/C (-0.434 eV) is smaller than that of Pt (-0.587 eV) (**Figs. 9d and e**). Compared with pure Pt, the d-band centre of PCPAF-HEI/C shifted downward, indicating that the Pt site of PCPAF-HEI/C was weaker for hydrogen adsorption, and the Pt-H binding energy was optimised. This prevents the excessive binding of hydrogen on the surface, thereby enhancing the HER activity (**Fig. 9f**).

Wang et al.^[61] synthesised HEI NPs with different degrees of ordering, namely highly ordered, partially ordered, and disordered Pt₄FeCoCuNi NPs, and evaluated their HER performance in a 1 M KOH aqueous solution. The highly ordered Pt₄FeCoCuNi NPs exhibited an overpotential of 20 mV at a current density of 10 mA cm⁻², which was significantly lower than those of the partially ordered, disordered Pt₄FeCoCuNi, and commercial Pt/C (32, 47, and 38 mV, respectively) (**Figs. 9g and h**). The highly ordered Pt₄FeCoCuNi has the smallest Tafel slope (31 mV dec⁻¹) (**Fig. 9h**), suggesting the faster kinetics in alkaline HER. The durability of the as-synthesised catalysts was assessed by chronopotentiometric measurements for over 50 h at a current density of 10 mA cm⁻². The order of stability was as follows: commercial Pt/C << disordered Pt₄FeCoCuNi NPs < partially ordered Pt₄FeCoCuNi NPs < highly ordered Pt₄FeCoCuNi NPs (**Fig. 9i**). The results indicate that both the activity and stability of the HER are correlated with the crystal structure of the Pt₄FeCoCuNi NPs. The superior activity of the highly ordered Pt₄FeCoCuNi NPs could be attributed to the synergistic effect between the alternating Pt columns, which promoted proton recombination, and the Fe/Co/Ni/Cu columns, which facilitated hydrolysis dissociation.

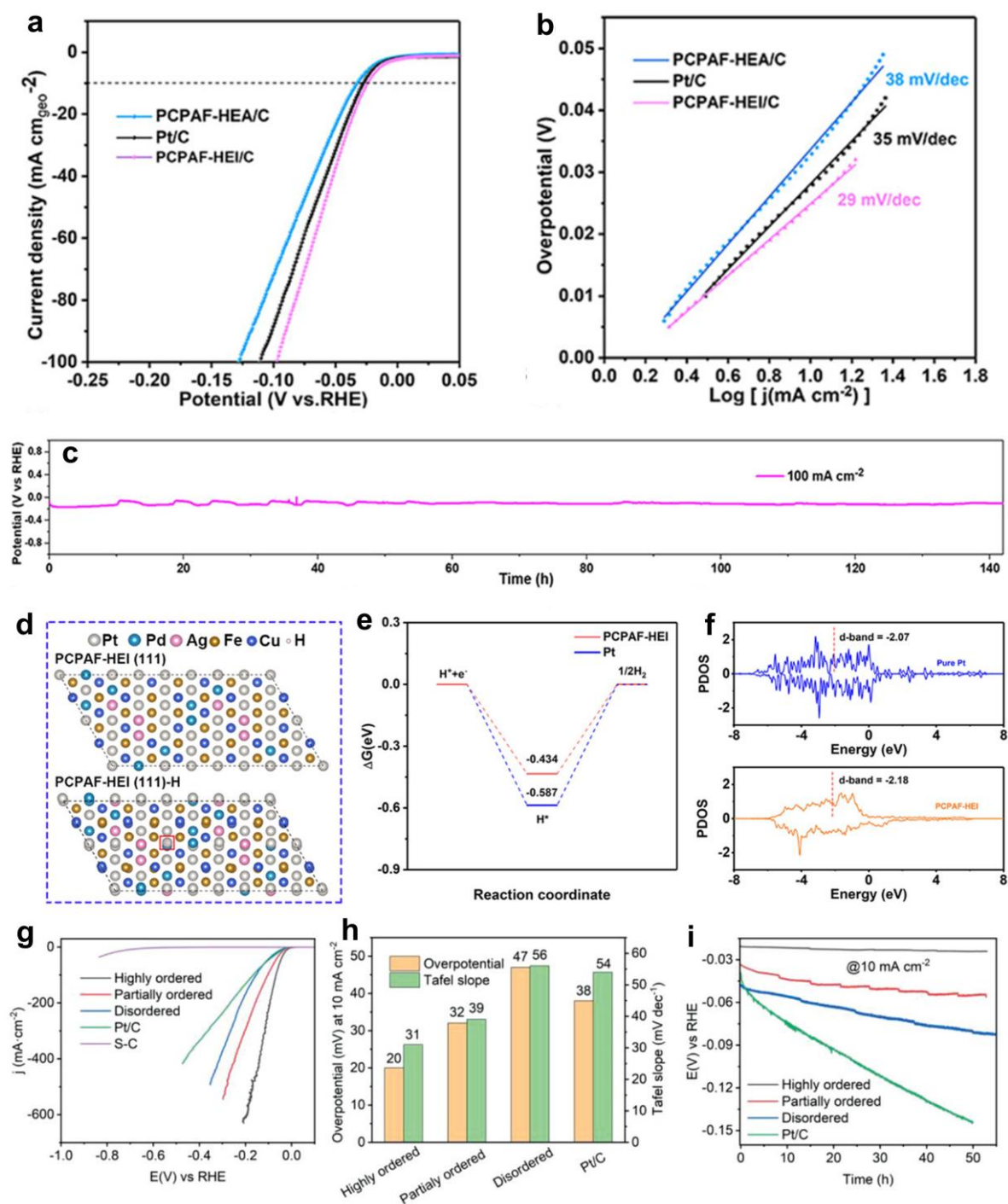


Fig. 9 (a) Linear sweep voltammetry (LSV) curves and (b) Tafel slopes of HEI- and HEA- PtCuPdAgFe HEI NPs/C and Pt/C. (c) Chronopotentiometry curve of PtCuPdAgFe HEI NPs/C at 100 mA cm^{-2} . (d) DFT model of PtCuPdAgFe HEI (111) surface and hydrogen atomic absorption at the Pt Site. The calculated (e) hydrogen-adsorption free energies ΔG_{H^*} and (f) Partial density of states (PDOS) of PtCuPdAgFe HEI and Pt. Reprinted with permission from ref. 60. Copyright 2024 Wiley-VCH. (g) LSV curves of Pt₄FeCoCuNi NPs with different degrees of ordering, Pt/C and bare S-C. (h) Histograms of overpotential and Tafel slope values and (i) Chronopotentiometry curves of Pt₄FeCoCuNi NPs with different degrees of ordering and Pt/C. Reprinted with permission from ref. 61. Copyright 2023 Wiley-VCH.

Liu et al.^[81] reported that the (FeCoNi)(RuPt)/CNFs catalyst showed outstanding HER performance in a 1.0 M KOH, delivering 200 mA cm^{-2} at an overpotential of only 54 mV with

a Tafel slope of 47.1 mV dec^{-1} (Figs. 10a and b), markedly surpassing other counterparts. Furthermore, in a mixed electrolyte of 1 M KOH and natural seawater,

(FeCoNi)(RuPt)/CNFs still maintained a low overpotential of 56 mV and an outstanding mass activity of $3.8 \text{ A mg}^{-1}(\text{PtRu})$, three times higher than that of commercial Pt/C ($1.3 \text{ A mg}^{-1}(\text{PtRu})$) (Figs. 10c and d), indicating excellent resistance to seawater ions. Electrochemical impedance spectroscopy (EIS) revealed a charge transfer resistance (R_{ct}) as low as $\sim 1.4 \Omega$ (Fig. 10e), demonstrating enhanced electron transfer kinetics. To further evaluate its practical applicability, an alkaline electrolyser was assembled using (FeCoNi)(RuPt)/CNFs as both anode and cathode. For comparison, a conventional Pt/C||RuO₂ system was also constructed. At a current density of 100 mA cm^{-2} , the (FeCoNi)(RuPt)/CNFs||(FeCoNi)(RuPt)/CNFs configuration exhibited a notably lower cell voltage of 1.69 V, compared to 1.98 V for the Pt/C||RuO₂ system (Fig. 10f), along with excellent long-term stability during continuous seawater electrolysis (Fig. 10g). In situ electrochemical Raman spectroscopy (Fig. 10h) further provided that the multiple active metal sites of the (FeCoNi)(RuPt) HEI NPs promote water dissociation and thereby enhance the HER process.

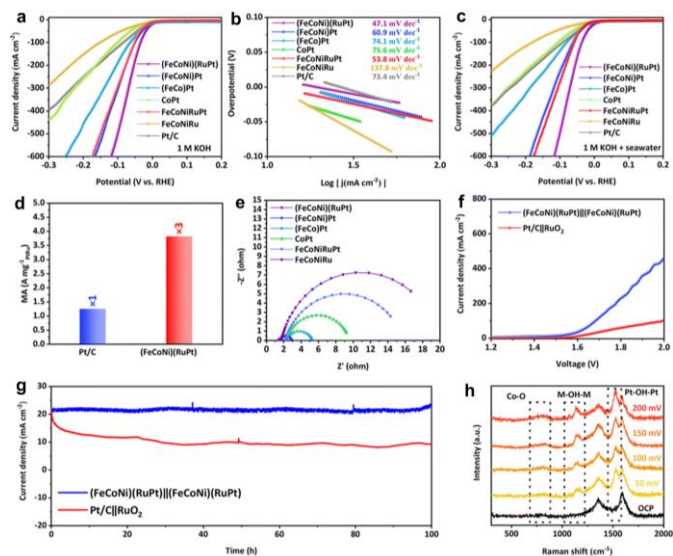


Fig. 10 (a) LSV curves and (b) Tafel slopes of (FeCoNi)(RuPt) and other catalysts in 1.0 M KOH. (c) LSV curves, (d) Mass activities at -0.1 vs. reversible hydrogen electrode (RHE) and (e) EIS curves at -0.03 vs. RHE of different catalysts in seawater containing 1.0 M KOH. (f) Polarization curves and (g) Chronopotentiometry tests of (FeCoNi)(RuPt)||[(FeCoNi)(RuPt)] and Pt/C||RuO₂ electrolyzers at 1.67 V in 1 M KOH + seawater. (h) In-situ electrochemical Raman spectroscopy of (FeCoNi)(RuPt) HEI NPs in seawater containing 1.0 M KOH. Reprinted with permission from ref. 81. Copyright 2025 The Royal Society of Chemistry.

4.2 NO₃RR

NH₃ is an important raw material for fertilisers and can be used as a support of H₂[98], which is of great importance in modern industries. Currently, the industrial production of NH₃ is mainly based on the traditional Haber–Bosch process.[99] However, the excessive release of NO₃⁻ caused by human use of NH₃ disrupts the natural nitrogen cycle. The electrochemical NO₃RR is a promising process for converting NO₃⁻ into the industrially

useful chemical—NH₃.^[5] However, NO₃RR generate multiple byproducts, such as nitrous acid (NO₂⁻), N₂, and hydroxylamine (NH₂OH) [100–103], necessitating the development of catalysts with high selectivity and activity. The theoretical potential of $E_{\text{NO}_3^-/\text{NH}_3}$ under alkaline conditions (pH 14) is $+0.69 \text{ V vs. RHE}$, [104,105] but the overpotential of NO₃RR is significantly increased due to its eight-electron and nine-proton transfer processes generating large kinetic barriers. Therefore, competitive HER is inevitable, reducing the selectivity for the conversion of NO₃⁻ to NH₃ and decreasing the Faraday efficiency (FE) of NH₃ production.[106] Therefore, the design of advanced NO₃RR electrocatalysts is urgently required. Currently, the exploration of catalysts for the NO₃RR is mainly focused on binary systems [107–109], while only two reports on HEI NPs.[110]

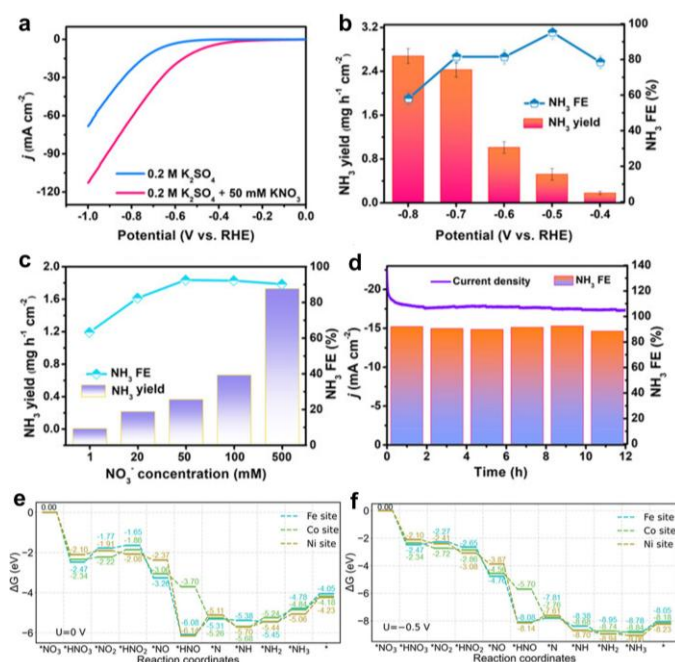


Fig. 11 (a) LSV curves of n-HEA NPs in 0.2 M K₂SO₄ solution and a mixture of 0.2 M K₂SO₄ solution and 50 mM KNO₃, respectively. The FE of NH₃ of n-HEA NPs (b) under different potential and (c) different NO₃⁻ concentration. (d) FE of NH₃ and chronopotentiometry curve of n-HEA NPs at -0.5 V vs. RHE . Distribution of Gibbs free energy ΔG on different metal sites at (e) voltage $U=0$ and (f) $U=-0.5 \text{ V}$. Reprinted with permission from ref. 110. Copyright 2024 Wiley-VCH.

Zhang et al. [110] introduced intermetallic NPs, FeCoNiAlTi, into the bulk HEA FeCoNiAlTi (defined as n-HEA) through an effective phase engineering strategy. The NO₃RR performance was measured in a 0.2 M K₂SO₄ solution, and a significant increase in the current density on the n-HEA sample was observed in the presence of KNO₃, indicating an excellent response to NO₃⁻ and great potential for the efficient conversion of NO₃⁻ (Fig. 11a). The FE of NH₃ achieved a maximum of 95.23% at -0.5 V vs. RHE , corresponding to an NH₃ yield of $0.52 \text{ mg h}^{-1} \text{ cm}^{-2}$ (Fig. 11b). Even when the concentration of KNO₃ was as low as 1 mM, the FE of the n-HEA FeCoNiAlTi was 63.25% (Fig. 11c). The FE of NH₃ decreased only slightly in a 12-hour potentiometric test at -0.5 V vs. RHE , indicating the outstanding

stability of n-HEA FeCoNiAlTi (**Fig. 11d**). The NO₃RR performance of the n-HEA FeCoNiAlTi was also investigated under alkaline conditions at pH 13. The FE of NH₃ reached a maximum of about 91.35% at -0.3 V vs RHE, corresponding to an NH₃ yield of 1.45 mg h⁻¹ cm⁻², which was significantly higher than that in neutral conditions. The stability of the n-HEA was also evaluated under a strongly alkaline condition at pH 14, and the FE of NH₃ of the n-HEA did not change significantly from the initial value after prolonged electrolysis. DFT calculations revealed that ordered FeCoNiAlTi has multiple active sites, including Fe, Co, and Ni sites (Co being the most active), and the relatively moderate metal-O bond strengths indicate that the reduction process was Sabatier-optimal (**Figs. 11e and f**).

Zhu et al. [79] explored the NO₃RR performance of Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}, Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}, and Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2} HEI NPs in a 1 M KOH solution with 0.1 M KNO₃ electrolyte. Among them, the Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} NPs exhibits the maximum current densities, the highest FE (a maximum of 98.8% at -0.30 V vs. RHE) and largest NH₃ yield rate within the potential range of 0 to -0.8 V vs. RHE (**Figs. 12a-c**). The Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} also possesses the lowest Tafel slope of 216.6 mV dec⁻¹, as well as the largest electrochemically active surface areas value of 61.60 mF cm⁻² (**Figs. 12d and e**). The long-term stability of Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} catalyst were also demonstrated (**Fig. 12f**). The electrochemical NO₃RR performance of binary ordered PtFe, quaternary ordered Pt_{0.6}Fe_{0.2}Co_{0.2}Ni_{0.2} was inferior to that of the quinary counterpart, highlighting the importance of multisite synergism in this process. And the ordered Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} HEI outperformed its disordered counterparts, likely due to the crucial role of isolated metal sites in enhancing NO₃RR activity. The Gibbs free energy ΔG of the catalysts was calculated by DFT, and the maximum ΔG values appeared in the *NO → *NOH step, with energy barriers of 0.23, 0.42 and 1.33 eV for Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}, Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2} and Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2}, respectively (**Fig. 12g**). The DFT results indicate that the excellent performance of the Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} catalyst is attributed to multisite synergies. The Pt-X bridge sites (where X represents Fe, Co, Ni, and Cu) facilitate optimal adsorption of NO_x species, while the site-isolated Pt atoms enhance H₂O adsorption, thereby promoting the formation of active *H.

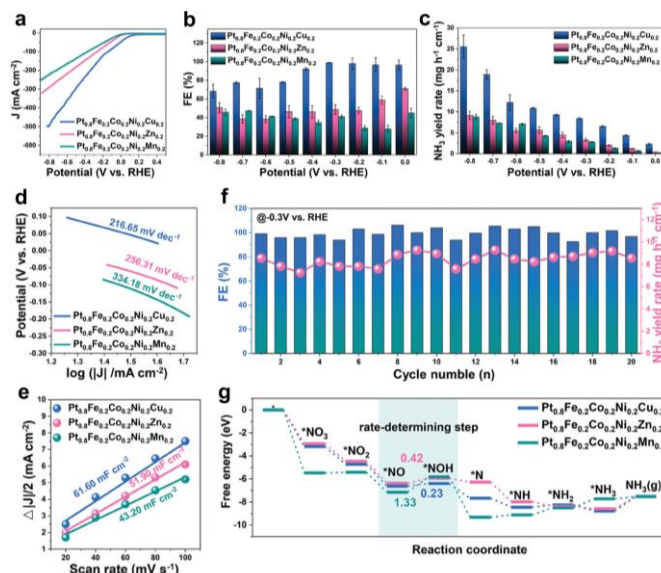
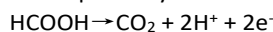


Fig. 12 (a) LSV curves, (b) the FEs, (c) NH₃ yield rates, (d) Tafel slopes and (e) calculate C_{dl} of the Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}, Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}, and Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2} HEI NPs in a 1 M KOH solution containing 0.1 M KNO₃. (f) Long-term stability test of Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2} at -0.3 V vs. RHE. (g) Free energy profiles for the (110) surface of the Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}, Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}, and Pt_{0.8}Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2} HEI NPs. Reprinted with permission from ref. 79. Copyright 2025 Wiley-VCH.

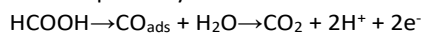
4.3 FAOR

DFAFCs hold great promise for application in diverse areas, including portable electronics, electric vehicles, and small household appliances, owing to their high energy density, simple system design, and enhanced safety. [111,112] At the anode, formic acid is oxidised to produce CO₂. The FAOR typically follows two different pathways: the direct pathway, in which HCOOH undergoes sequential dehydrogenation processes to ultimately produce CO₂, and the indirect pathway, in which HCOOH dehydrates to form CO_{ads} as an intermediate, which is then oxidised to CO₂. [113,114]

Direct pathway:



Indirect pathway:



The direct pathway is preferred over the indirect pathway because the intermediate CO_{ads} in the indirect pathway can result in catalyst poisoning. Pd- and Pt-based catalysts are effective FAOR catalysts; [112,115] however, their low mass activity and susceptibility to CO poisoning hinder their industrial application. [116] Thus, the development of more stable and efficient FAOR catalysts is critical.

Zhan et al. [117] successfully obtained PtBiPbNiCo high-entropy alloy hexagonal nanoplates (HEA HPs) with ordered PtBiPb medium-entropy cores and PtBiNiCo multi-element shells. The current of the HEA HPs/C was much higher than that of the binary PtPb HPs/C and commercial Pt/C (**Fig. 13a**). And HEA HPs/C exhibited excellent FAOR performance, with a mass activity of 7.1 A mg_{Pt}⁻¹ and specific activity of 27.2 mA cm⁻² at

0.55 V vs RHE, which were 3 times higher than that of Pt/Pb HPs/C (2.6 A mg_{Pt}⁻¹, 9.0 mA cm⁻²) and 56 and 133 times higher than that of commercial Pt/C (0.127 A mg_{Pt}⁻¹, 0.205 mA cm⁻²), respectively (**Fig. 13b**). The FAOR activity of the HEA HPs/C exceeded that of all Pt/Pd-based catalysts reported to date (**Fig. 13c**). Furthermore, the potential of HEA HPs/C for practical application in DFAFC devices was investigated using commercial Pt/C as the cathode catalyst and HEA HPs/C as the anode catalyst (**Fig. 13d**). HEA HPs/C exhibited excellent power density (highest 321.2 mW cm⁻²) (**Fig. 13e**) and stability (**Fig. 13f**) (power density decay 55.1% after 30 h under 0.4 V vs. RHE) for DFAFC, which was significantly superior to that of commercial Pd/C. In situ Fourier transform infrared (FTIR) spectroscopy demonstrated that HEA HPs/C significantly reduced CO* adsorption (**Fig. 13g**), accelerated CO* oxidation, and promoted the dehydrogenation of formic acid. DFT calculations of the Gibbs free energy of the dehydrogenation and dehydration pathways indicated that the excellent FAOR performance of the HEA HPs can be ascribed to the lowered Gibbs free energy of the direct oxidation pathway as well as the inhibition of the indirect oxidation pathway (**Figs. 13h–j**).

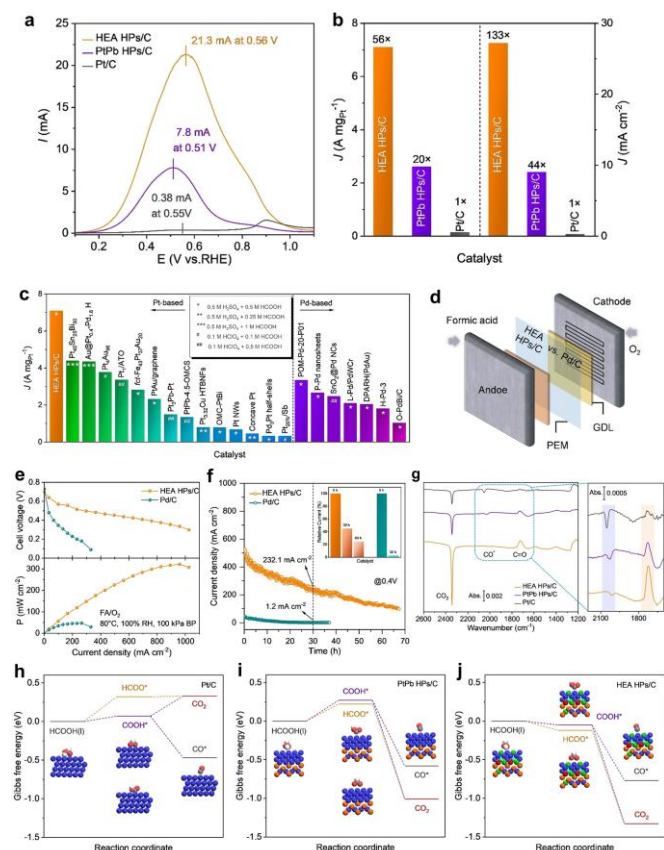


Fig. 13 (a) CV curves and (b) mass activity (left) and specific activity (right) of PtBiPbNiCo HPs/C, PtPb HPs/C and Pt/C. (c) A comparison of the mass activity of PtBiPbNiCo HPs/C with some reported FAOR catalysts. (d) The DFAFC device with PtBiPbNiCo HPs/C as the anode catalyst. (e) The power density and steady-state polarisation curves and (f) current density under 0.4 V vs. RHE for DFAFC of PtBiPbNiCo HPs/C and Pd/C. The inset in (f) shows the current attenuation. (g) In situ FTIR of PtBiPbNiCo HPs/C, PtPb HPs/C and Pt/C in a mixture of 0.1 M H₂SO₄ and 0.05

M HCOOH. The calculated Gibbs free energy for FAOR of (h) Pt/C, (i) PtPb HPs/C, and (j) PtBiPbNiCo HPs/C. Reprinted with permission from ref. 117. Copyright 2023 Wiley-VCH.

Shen et al.^[74] constructed ultrasmall 2 nm (PtPdIrRu)₂FeCu HEI NPs and evaluated their FAOR performance in a mixed solution of 0.5 M HCOOH and 0.5 M H₂SO₄. The specific activity of HEI/C was approximately an order of magnitude higher than that of Pt/C, and the mass activity of HEI/C was 1.7 and 4.4 times higher than that of Pt₂FeCu/C and Pt/C at 0.6 V vs. RHE, respectively. Based on the in-situ IR spectra for HEI NPs/C, no significant CO* signal was observed during FAOR, indicating that the electrooxidation of HCOOH mainly proceeded via the direct pathway, whereas on Pt/C, a top (CO_L) and bridge (CO_B) CO* pattern appeared, suggesting that the oxidation was carried out via an indirect pathway. The ternary Pt₂FeCu/C lost most of its activity after only 3,000 s in the chronoamperometry at 0.6 V vs RHE, but HEI NPs/C maintained a considerable current density even after 10,000 s of measurement, showing the superior stability of the (PtPdIrRu)₂FeCu NPs. DFT calculations showed that the adsorption energy (*E*_{ad}) of CO* at the Pt site of HEI (110) was much smaller in absolute value compared with that of Pt (111). This can be attributed to the electronic effect, namely a decrease in the binding strength of the adsorbate as the d-band centre downshifts. Meanwhile, CO* could easily diffuse over the hollow and bridge sites on the Pt (111) surface. However, on the (110) surface of the HEI, the diffusion of CO* would require high energy barriers between the different sites. Therefore, the adsorption of CO* on the HEI was weakened, and diffusion was slow, protecting the active sites from deactivation.

4.4 AOR

Alcohols such as methanol, ethanol, and glycerol are also important potential chemical fuels for fuel cells, which generally provide a higher energy density and are environmentally friendly.^[118] AOR is the anode reaction in DAFCs. However, the AOR is a complicated reaction which involves multiple electron transfers and intermediates, resulting in slower kinetics and incomplete oxidation.^[119,120] For example, the ethanol oxidation reaction (EOR) involves two pathways, namely, C1 and C2 pathways. In the C1 pathway, 12 electrons are transferred, with CO₂ as the product, while in the C2 pathway, 2 or 4 electrons are transferred, producing acetaldehyde or acetic acid. The C2 process can also produce CO, causing catalyst poisoning. Therefore, increasing the selectivity of the C1 pathway is expected to improve the catalytic activity of the EOR.

Wang et al.^[72] reported novel structurally ordered PtRhFeNiCu HEI NPs that exhibited superior catalytic activity for EOR. The EOR activity was measured in a mixture of 0.2 mol/L CH₃CH₂OH and 0.1 mol/L HClO₄ (**Fig. 14a**). During the electrochemical measurements, two peaks appeared in the forward scan: peak f1 corresponded to the oxidation of ethanol to acetic acid, acetaldehyde, and CO₂, whereas peak f2 indicated acetic acid production. In the reverse scan, peak b represents the oxidation of the carbonaceous intermediates. The *I*_{f1}/*I*_{f2} ratio evaluates the catalyst activity or C-C bond cleavage ability of the EOR, while the *I*_{f1}/*I*_b ratio indicates CO intermediate tolerance.^[121–123] The PtRhFeNiCu HEI NPs showed

the highest I_{f1}/I_{f2} and I_{f1}/I_b values (**Fig. 14b**), indicating excellent C-C bond cleavage ability and CO intermediate tolerance compared with the HEA NPs. The HEI NPs also displayed the lowest CO removal onset potential, outperforming the HEA NPs and Pt/C. And the mass and specific activities of HEI NPs were 914 mA/mg_{Pt} and 1.40 mA/cm²_{Pt}, respectively, higher than those of HEA NPs (578 mA/mg_{Pt} and 1.32 mA/cm²_{Pt}, respectively) and Pt/C (202 mA/mg_{Pt} and 0.36 mA/cm²_{Pt}, respectively) (**Fig. 14c**). The HEI NPs exhibited a high current density and excellent stability over 50,000 s of chronoamperometric measurement at 0.6 V vs. RHE (**Fig. 14d**). The HEI NPs were then used as anodes in fuel cells to evaluate their activity under practical operating conditions. The HEI NPs achieved a power density up to 47.50 mW/cm² in direct ethanol fuel cells (DEFCs), surpassing HEA (38.10 mW/cm²) by 1.25 times and Pt/C (16.0 mW/cm²) by 2.97 times. The DFT calculations revealed that the structural stability of the PtRhFeNiCu HEI was higher than that of its corresponding HEA (**Fig. 14e**). The d-band centre of HEI, -2.28 eV, was lower than that of HEA, -2.13 eV, which could weaken the adsorption of CO intermediates and thus inhibit CO poisoning. In addition, PtRhFeNiCu HEI requires a lower energy barrier of 0.29 eV for C-C bond cleavage compared to 0.49 eV for HEA (**Fig. 14f**), which is attributed to the ordered structure of HEI, which reduces the energy barrier by modifying the adsorption configuration of the key intermediate.

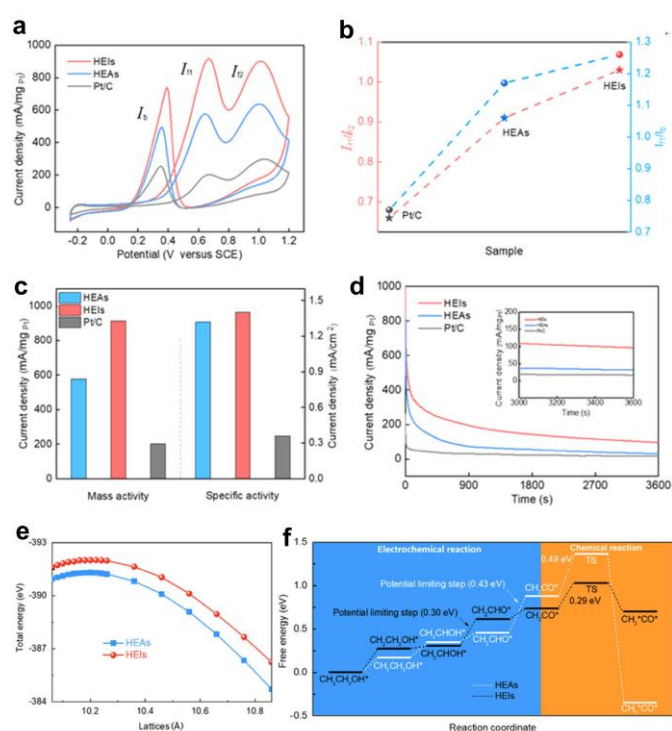


Fig. 14 (a) EOR activities of the HEA- and HEI- PtRhFeNiCu NPs, and Pt/C in a mixture of 0.1 mol/L HClO₄ and 0.2 mol/L CH₃CH₂OH (N₂-saturated). (b) The ratios of I_{f1}/I_b and I_{f1}/I_{f2} derived from the CV curves of the HEA- and HEI- PtRhFeNiCu NPs, and Pt/C. (c) Mass and specific activities of the HEA- and HEI- PtRhFeNiCu NPs, and Pt/C. (d) Chronoamperometry curves of the HEA- and HEI- PtRhFeNiCu NPs, and Pt/C at 0.6 V vs. RHE. (e) DFT calculation of total energy for HEA- and HEI- PtRhFeNiCu with different lattices. (f) The calculated free energy of EOR

process on HEA- and HEI- PtRhFeNiCu NPs. Reprinted with permission from ref. 72. Copyright 2023 Wiley-VCH.

Chen et al.^[86] synthesised PtRhBiSnSb HEI nanoplates by one-pot method and investigated their AOR activity in a 1.0 M KOH solution. PtRhBiSnSb HEI nanoplates exhibited the highest mass activities for methanol oxidation reaction (MOR), EOR, and glycerol oxidation reaction (GOR), achieving 19.529 A mg⁻¹_{Pt+Rh}, 15.558 A mg⁻¹_{Pt+Rh}, and 7.535 A mg⁻¹_{Pt+Rh}, respectively, which were superior to those of PtBiSnSb nanoplates and Pt/C (**Figs. 15a–c**). PtRhBiSnSb and PtBiSnSb nanoplate retained 70.2% and 62.7% of their initial current densities at 0.85 V vs RHE, respectively, while Pt/C retained only 23.1% of its initial current density after 5000 cycles in a mixture of 1.0 M KOH and 1.0 M CH₃OH solution (**Fig. 15d**). Chronoamperometric measurements of the MOR at 0.7 V vs RHE for 20,000 s showed the excellent long-term stability of the PtRhBiSnSb HEI nanoplates. CO stripping experiments showed that the oxidation peaks of CO (at around 0.7 V vs. RHE) absorbed on PtRhBiSnSb (**Fig. 15e**) and PtBiSnSb HEI nanoplates were significantly suppressed, indicating their tolerance to CO. In situ FTIR also revealed that the MOR on the PtRhBiSnSb HEI nanoplates occurred via a CO-free pathway (**Fig. 15f**). This was due to the isolation of surface Pt sites, absence of continuous Pt sites, and increased Pt-Pt distance, which reduced or even eliminated CO adsorption on the HEI NPs. DFT calculations indicated that the incorporation of Rh into the PtRhBiSnSb HEI nanoplates further improved their activity. Compared with PtBiSnSb, the d-band centre of PtRhBiSnSb increased significantly after the introduction of Rh (**Fig. 15g**), indicating that the efficiency of electron transfer was improved. The adsorption of CH₃OH and CO₂ on the PtRhBiSnSb HEI nanoplates was enhanced compared with that on the PtBiSnSb HEI nanoplates (**Fig. 15h**). Additionally, the optimised electronic structure of the PtRhBiSnSb HEI nanoplates resulted in a higher energy barrier for the CO pathway in the MOR, leading to higher selectivity towards the CO₂ pathway (**Figs. 15i and j**).

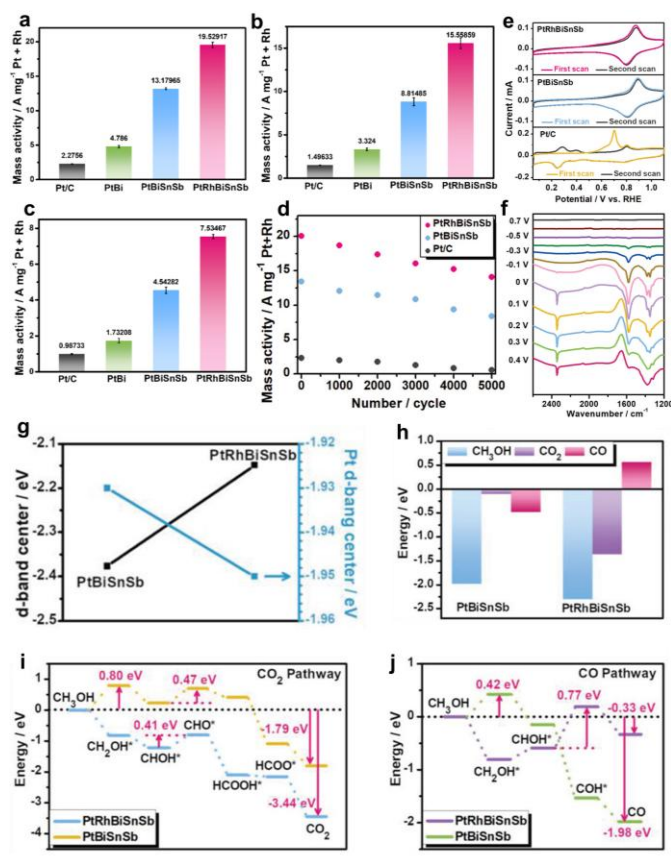


Fig. 15 Mass activity histograms of (a) MOR, (b) EOR and (c) GOR for PtRhBiSnSb, PtBiSnSb, PtBi HEI nanoplates and Pt/C in a 1.0 M KOH solution (Ar-saturated). (d) Mass activity of different catalysts at different numbers of cycles. (e) CO stripping curves of different catalysts (scan rate: 50 mV s⁻¹). (f) In-situ FTIR spectra of PtRhBiSnSb HEI nanoplates (a mixture of Ar-saturated 1.0 M KOH and 1.0 M CH₃OH). (g) d-band centres of PtRhBiSnSb and PtBiSnSb HEI nanoplates. (h) Adsorption energies of CH₃OH, CO₂ and CO on PtRhBiSnSb and PtBiSnSb HEI nanoplates. Comparison of reaction energies for (i) the CO₂ pathway and (j) the CO pathway during the MOR process on PtRhBiSnSb and PtBiSnSb HEI nanoplates. Reprinted with permission from ref. 86. Copyright 2022 Wiley-VCH.

Hao et al. [80] evaluated the ethylene glycol oxidation reaction (EGOR) performance of (PtIr)(FeMoBi) HEI NPs in the mixture of 1 M KOH and 1 M EG. According to the CV curves, (PtIr)(FeMoBi) showed a wider active potential (0.35–1.10 V vs. RHE) and higher oxidation current density (208.2 mA cm⁻²) than (PtIr)(FeMo), PtIrFeMoBi, and commercial Pt/C catalysts (**Fig. 16a**). CO-stripping experiments demonstrated the absence of distinct CO oxidation peaks on (PtIr)(FeMoBi) (**Fig. 16b**), suggesting strongly suppressed *CO oxidation due to the isolated Pt sites in its ordered structure. The (PtIr)(FeMoBi) catalyst exhibited a mass activity of 5.2 A mg_{Pt}⁻¹ for EGOR, outperforming (PtIr)(FeMo) (2.4 A mg_{Pt}⁻¹), PtIrFeMoBi (2.1 A mg_{Pt}⁻¹), and commercial Pt/C (1.4 A mg_{Pt}⁻¹) (**Fig. 16c**). Chronoamperometric measurements were performed to assess the long-term durability of (PtIr)(FeMoBi), revealing its excellent resistance to poisoning (**Fig. 16d**). The alternating carbonophilic Pt/Ir and oxygenophilic Fe/Mo sites on the (PtIr)(FeMoBi) surface promote the co-adsorption of EG and OH species. This well-organized distribution creates a uniform

coordination environment that enhances selectivity toward GA, minimizes the competition between *EG and *OH adsorption, and accelerates the overall reaction kinetics. DFT results indicate that the Pt site in (PtIr)(FeMoBi) exhibits a lower energy barrier (0.94 eV) for the CH₂OH–CO → CH₂OH–COOH step compared to pure Pt (1.49 eV) (**Fig. 16e**). Additionally, Fe sites show the lowest barrier for the dehydrogenation step. The synergistic effect between Pt and Fe sites enhances activity and selectivity by alleviating competitive adsorption of EG and OH. Bader charge analysis shows electron depletion at Pt sites of HEI NPs (10.62 e vs. 11.94 e for pure Pt), leading to a downshifted d-band center (–2.540 eV, Pt: –1.932 eV) (**Fig. 16f**), which weakens intermediate adsorption and reduces the barrier for CH₂OH–COOH formation (1.13 eV) (**Fig. 16g**).

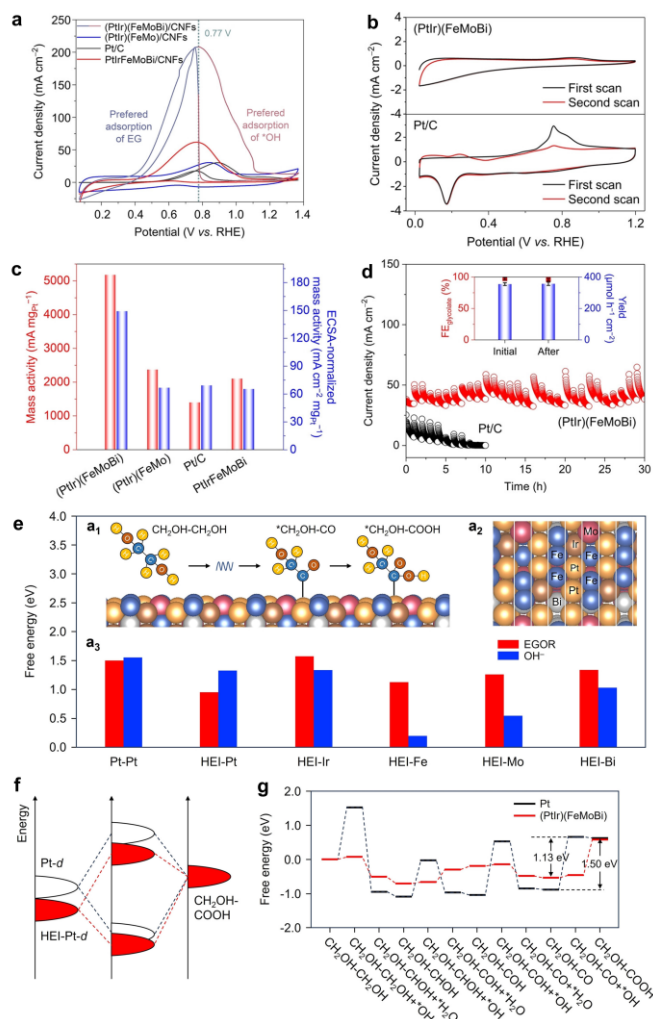


Fig. 16 (a) CV curves of Pt/C, PtIrFeMoBi, (PtIr)(FeMo) and (PtIr)(FeMoBi) in 1 M KOH containing 1 M EG. (b) CO-stripping experiments of Pt/C and (PtIr)(FeMoBi) in 1 M KOH. (c) Mass activity and ECSA-normalized activity for EGOR. (d) Chronoamperometric measurements of (PtIr)(FeMoBi) and Pt/C was evaluated at 0.77 V vs. RHE. The inset presents the FE_{GA} and GA yield of (PtIr)(FeMoBi) before and after the durability test. (e) DFT calculations. (a₁) Illustration of the EGOR mechanism on the (PtIr)(FeMoBi) surface. (a₂) Surface elemental distribution of (PtIr)(FeMoBi). (a₃) Energy barriers for rate-determining step CH₂OH–CO → CH₂OH–COOH at Pt sites on pure Pt and various sites on (PtIr)(FeMoBi). (f) d-band centers of Pt in pure Pt and (PtIr)(FeMoBi). (g) Free energy diagrams of the involved

intermediates on Pt and (PtIr)(FeMoBi) surfaces. Reprinted with permission from ref. 80. Copyright 2025 Wiley-VCH.

4.5 ORR

The ORR is a fundamental chemical process that occurs at the cathode of a fuel cell. ORR involves either two-electron ($2e^-$) or four-electron ($4e^-$) reduction, that is, two-electron reduction to produce H_2O_2 , four-electron reduction of oxygen to H_2O in acidic media, or reduction of oxygen to OH^- in neutral or alkaline media. The H_2O_2 produced by the two-electron reduction is unstable and is further reduced to H_2O . The four-electron reaction involves the transfer of multiple electrons as well as a multistep reaction, with each step requiring different energy barriers to be overcome, resulting in very slow ORR kinetics. [124,125] In addition, the ORR relies on rare precious metal catalysts, such as Pt. Therefore, increasing efficiency and reducing costs are the directions of ORR research.

Since 2022, there have been several reports on HEI NPs for ORR, and they have demonstrated excellent performance. ORR is also the most widely researched electrocatalytic reaction for HEI NPs. Reports on the ORR activity and stability of HEI NPs over the past few years are listed in **Table 3**.

Feng et al. [59] synthesised ordered PtIrFeCoCu HEI (PIFCC-HEI) NPs and evaluated their ORR performance in an O_2 -saturated 0.1 M $HClO_4$ solution. The half-wave potential ($E_{1/2}$) of PIFCC-HEI/C was 0.894 V vs. RHE, which is higher than that of commercial Pt/C (0.853 V vs. RHE) (**Fig. 17a**). The lower Tafel slope of PIFCC-HEI/C (63.5 mV dec^{-1}) compared to that of commercial Pt/C (75.6 mV dec^{-1}) demonstrates its superior ORR kinetics. The mass activity of PIFCC-HEI/C reached $7.14 \text{ A mg}_{\text{noble metal}}^{-1}$ at a potential of 0.85 V vs RHE, which was 20.4 times higher than that of commercial Pt/C ($0.35 \text{ A mg}_{\text{Pt}}^{-1}$) and 2.0 times higher than that of PIFCC-HEA/C ($3.03 \text{ A mg}_{\text{noble metal}}^{-1}$), respectively (**Fig. 17b**). No significant drop was observed in the current density of PIFCC-HEI/C during the 60 h chronopotentiometric measurement (**Fig. 17c**). In addition, PIFCC-HEI/C exhibited only a 9-mV reduction in $E_{1/2}$ after 60,000 cycles, significantly outperforming commercial Pt/C, which experienced a 49-mV loss (**Fig. 17d**). PIFCC-HEI/C was used as the cathode, with commercial Pt/C as the anode, for the ORR in proton exchange membrane fuel cell (PEMFC) applications. PIFCC-HEA/C achieved a current density of 4.25 A cm^{-2} at 0.4 V in practical H_2/O_2 fuel cells, significantly higher than that of commercial Pt/C (3.67 A cm^{-2}) (**Fig. 17e**). It maintained stable operation at a current density of 1 A cm^{-2} for 80 h, with only a 1% degradation in operating voltage (**Fig. 17f**). DFT calculations suggested that the enhanced ORR performance of the HEI NPs mainly originated from the ultra-high activity of the (001)

crystalline facet, which provided the lowest activation energy barrier (**Figs. 17g and h**) and an optimal downward shift of the d-band centre for the rate-limiting step. Typically, the ORR activity of the (001) crystalline facet in metal catalysts is much lower than that of the (111) crystalline facet in $HClO_4$ electrolytes. By constructing a multi-element ordered PIFCC HEI, the (001) facet was transformed into an ultra-highly active facet. Thus, both the active (111) and (001) facets contributed to the excellent ORR activity of PIFCC-HEI.

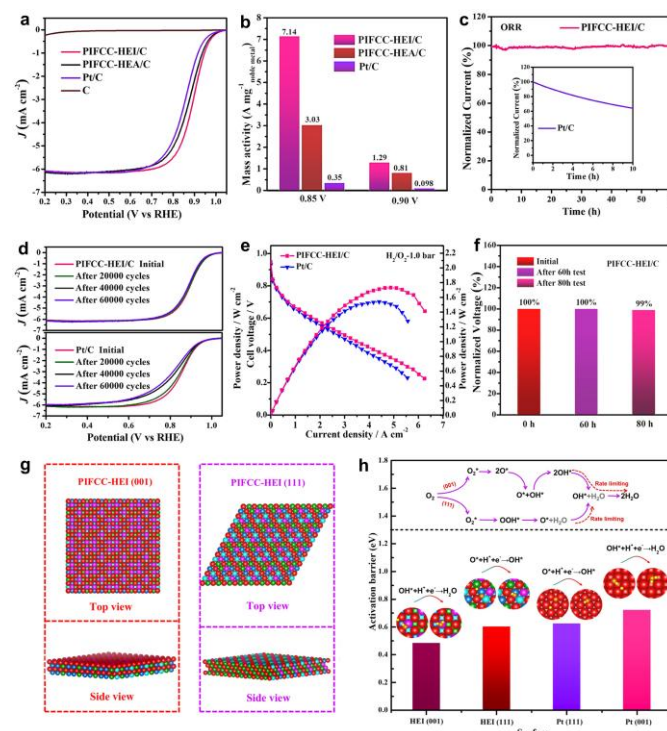


Fig. 17 (a) Polarization curves of HEI- and HEA- PtIrFeCoCu NPs/C, commercial Pt/C and pure carbon measured in a 0.1 M O_2 -saturated $HClO_4$ solution. (b) Mass activities of HEI- and HEA- PtIrFeCoCu NPs/C and commercial Pt/C at 0.85 and 0.9 V vs. RHE. (c) Chronopotentiometry curves of PtIrFeCoCu HEI NPs/C and commercial Pt/C at a constant potential. (d) Polarisation curves of PtIrFeCoCu HEI NPs/C and commercial Pt/C before and after different numbers of CV cycles. (e) Polarisation and power density curves for PEMFC applications with PtIrFeCoCu HEI NPs/C and commercial Pt/C as the cathode, respectively. (f) The voltage declines in PEMFC application at different times. (g) The top and side views of (111) surface (right) and (001) surface (left) of PtIrFeCoCu-HEI. (h) The activation barriers evaluated on the (001) and (111) surface of PtIrFeCoCu-HEI and Pt. Reprinted with permission from ref. 59. Copyright 2023 American Chemical Society.

Table 3. Comparisons of electrocatalytic ORR activity and stability of HEI NPs reported in recent literature

Element	Solution	Mass loading ($\text{mg}_{\text{noble metal}} \cdot \text{cm}^{-2}$)	$E_{1/2}$ (V)	Tafel slope (mV decade^{-1})	ECSA ($\text{m}^2 \text{ g}_{\text{noble metal}}^{-1}$) / TOF (s^{-1})	Mass activity ($\text{A mg}_{\text{noble metal}}^{-1}$) @ 0.9 V vs. RHE	The number of transferred electrons	Decay of $E_{1/2}$ (mV)/ Cycle	Ref.
PtIrFeCoCu	0.1 M $HClO_4$	0.0049	0.894	63.5	31.7	1.29	-	2/20k 6/40k	59

								9/60k	
Pt ₄ FeCoCuNi	0.1 M HClO ₄	0.0086	0.943	51.5	-	3.78	3.98	7/30k	61
PtFeCoNiCuZn	0.1 M HClO ₄	0.0300	0.906	59	69.2	2.403	4.0	1/10k	71
PtPdFeCoNi	0.1 M KOH	0.0250 (all metal)	0.910	60.2	62.6	0.63	≈4.0	-	68
Pt(FeCoNiCuZn) ₃	0.1 M HClO ₄	0.0250	0.922	-	52.3	0.70	≈4.0	2/30k	73
CoFeNiCuPd	0.1 M KOH	0.0177	0.90	55	0.049 s ⁻¹	2.037	≈4.0	10/10k	77

5. Conclusions and outlook

HEI NPs combine the unique advantages of HEA and intermetallic compounds while leveraging on the high surface activity and multifunctional properties of nanostructures. Over the past few years, HEI NPs have attracted significant attention and shown excellent performance in electrocatalytic reactions. In this review, we summarise the research achievements in HEI NPs in recent years, focusing on their synthesis methods and applications in electrochemical catalysis.

Currently, the synthesis of HEI NPs involves methods such as wet chemical reduction and calcination, impregnation-reduction, and one-pot methods. Typically, a relatively high temperature is required to achieve an ordered structure during synthesis. However, high temperatures often lead to particle aggregation, which negatively affects the subsequent catalytic performance. Therefore, improving controllability during the preparation process is a key focus for future research. Technologies such as the multifunctional template method can be developed to control the morphology (e.g., core-shell, hollow, nanowire) and size distribution of HEI NPs, thereby optimising their specific surface areas and active sites. Different types of structures, including core-shell structures, hollow NPs, nanosheets, and nanowires, can be explored to further enhance their catalytic properties. Additionally, rapid synthesis techniques based on microwave heating can be developed to reduce reaction time and energy consumption.

Understanding the relationship between the structure and properties of HEI NPs is the key to optimising their functionality. In-situ characterisation techniques such as in-situ TEM, in-situ XRD, and in-situ FTIR can be used to study the dynamic evolution of HEI NPs during the reaction process and provide theoretical guidance for catalysis and functional optimisation. Theoretical calculations and machine learning can accelerate the research on HEI NPs. DFT calculations can be used to select novel HEI NPs systems and predict their structural stabilities and catalytic performances. Machine-learning models can be used to rapidly select constituent combinations with potentially superior performance.

The exploration of HEI NPs in catalysis is still at an early stage, and the current applications of HEI NPs in electrochemical catalysis have mainly focused on the HER, ORR, FAOR, and NO₃RR, while the exploration of HEI NPs in other electrochemical reactions, such as the OER and CO₂ reduction reaction, is still scarce. Therefore, investigating these application areas is highly meaningful and holds significant potential for future research. In addition, current research on HEI NPs has mainly focused on electrocatalysis and thermocatalysis, whereas there has been no research on the application of HEI NPs in photocatalysis. Multifunctional

catalysts with combined photocatalytic, electrocatalytic, and thermocatalytic properties could also be explored for application in complex energy systems.

Particularly, with the improvement and innovation of synthesis methods and characterisation techniques, and a deeper understanding of the reaction mechanism, HEI NPs are expected to become the next generation of high-performance and multifunctional catalytic materials.

Conflicts of interest

No conflicts to declare.

Acknowledgements

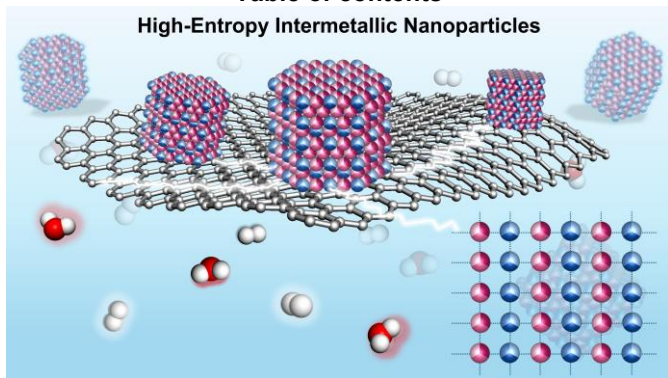
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Table of contents**High-Entropy Intermetallic Nanoparticles**

HEI NPs are promising catalysts combine the ordered intermetallic structures with the compositional complexity of high-entropy alloys. This review summarises the achievements of HEI NPs in recent years, with a focus on their synthesis methods and applications in electrochemical catalysis.