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Article

Keywords: electrocatalysts, hydrogen evolution reaction (HER)

Posted Date: February 5th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-145497/v1>

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Engineering sub-2 nm ultrasmall high-entropy alloy nanoparticles with extremely superior performance for hydrogen evolution catalysis

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Abstract

The development of intrinsically effective and low-cost catalysts is critical for the potential large-scale applications of electrocatalytic hydrogen production. Although various electrocatalysts have demonstrated high activities for hydrogen evolution reaction (HER), it remains a formidable challenge to develop an extremely efficient and durable catalyst for HER, especially in acidic media. Here, we report quinary ultrasmall NiCoFePtRh high-entropy alloy (us-HEA) nanoparticles (NPs) with extremely superior performance for HER. The us-HEA NPs are well dispersed on the carbon supports, with an average diameter of 1.68 nm, which is the smallest size in the reported HEAs. The us-HEA/C achieves an ultrahigh mass activity of 28.3 A mg⁻¹_{noble metals} (much higher than that of other reported advanced catalysts) at -0.05 V (vs the reversible hydrogen electrode, RHE) for HER in 0.5 M H₂SO₄ solution, which is 40.4 and 74.5 times higher than those of the commercial Pt/C and Rh/C catalysts, respectively. Moreover, the us-HEA/C demonstrates the highest reported turnover frequency of 30.1 s⁻¹ at 50 mV overpotential (41.8 times higher than that of the Pt/C catalyst) and excellent stability with no decay after 10,000 cycles. Both operando X-ray absorption spectroscopy and theoretical calculations reveal the true active sites and a synergistic effect among five elements, which endow us-HEA/C with significantly enhanced HER activity. This work not only provides a general and facile strategy for synthesizing us-HEA NPs, highlights HEAs as sufficiently advanced materials in energy electrocatalysis, but also acts as a guidance for elucidating the actual reaction process and catalytic mechanism of complex multi-element systems.

Introduction

Electrocatalytic water splitting is universally considered as an efficient and available technology to produce hydrogen fuel for renewable energy storage^{1,2}. Hydrogen production can achieve an ultrahigh hydrogen purity of 99.995%, excellent energy efficiency and fast kinetics process, especially in acidic media^{1,3}. Pt is generally regarded as the most effective electrocatalysts for the hydrogen evolution reaction (HER). However, Pt suffers from the high cost, scarcity, and poor electrochemical durability, preventing the widespread adoption of electrocatalytic hydrogen production^{4,5}. Thus, the design of highly efficient, low cost, and stable electrocatalysts for acidic HER is quite urgent.

To date, numerous reports have explored advanced electrocatalysts for HER. For instance, changing the dimensions of Pt from bulk to nanoparticle⁶, nanowire⁷, nanoplate⁸, or nanoframe⁹ can expose more active sites and increase the atomic utilisation efficiency of Pt. Alloying Pt with non-noble metals to fabricate binary or ternary alloys can reduce the use of Pt and tune the electronic structure^{10,11}. Single-atom catalysts (SACs) have been extensively investigated for HER due to their dramatic atom utilisation efficiency and ultrahigh mass activity^{12,13}. Non-noble metals and metal-free

nanomaterials have also been employed due to their low cost and favorable catalytic performance^{5,14,15}. Even though the above-mentioned catalysts appear promising, they demonstrate single electronic structure, high percentage of Pt, poor specific activity and long-term stability, or high overpotentials and undesirable structural destruction, respectively. These catalysts still cannot meet the necessary requirements for practical use in acidic media. Overall, major challenges still remain for research efforts focused on seeking other kinds of practical HER catalysts with extremely superior performance.

High-entropy alloys (HEAs) have demonstrated significant potential applications in many fields due to their unique and fascinating properties¹⁶⁻²⁰. Thus, HEAs have recently garnered increased attentions and become one of the hottest materials. Given their tunable composition, electronic structure, and significant stability in corrosive media, HEAs highly meet the necessary requirements of becoming advanced electrocatalysts. However, HEAs have only recently been researched in electrocatalysis²¹⁻²⁵, and the characteristics and properties are gradually investigated and disclosed. But the current HEA catalysts are suffering from various

challenges. For instance, the synthesis methods of HEAs are rather complex and hardly large-scale, the structural information of HEA catalysts has not been deeply revealed, the potential catalytic performance of HEAs have not been sufficiently explored, and the complicated catalytic mechanism of HEAs has not been clearly clarified. Therefore, more rational design of HEAs is urgently needed to support them as sufficiently advanced electrocatalysts, accelerating the research of HEAs in energy-related applications.

Herein, we employ a general and facile chemical co-reduction method to fabricate carbon-supported ultrasmall NiCoFePtRh high-entropy alloy (us-HEA) NPs. The us-HEA NPs exhibit a uniform distribution on carbon supports and an average particle size of 1.68 nm, which is the smallest size in the reported HEAs. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and X-ray absorption fine structure (XAFS) measurements reveal the atomic structure, electronic structure, and coordinational structure of us-HEAs. As an electrocatalyst for HER, us-HEA/C achieves an ultrahigh mass activity of $28.3 \text{ A mg}^{-1}_{\text{ noble metals}}$ (much higher than that of other reported advanced catalysts) at -0.05 V (vs the reversible hydrogen electrode, RHE) in $0.5 \text{ M H}_2\text{SO}_4$ solution, which is 40.4 times and 74.5 times higher than those of commercial Pt/C and Rh/C catalysts, respectively. Moreover, the us-HEA/C exhibits the highest reported turnover frequency (TOF) of 30.1 s^{-1} at

50 mV overpotential (41.8 times higher than that of the Pt/C catalyst) and excellent stability with no decay after 10,000 cycles. Both operando X-ray absorption spectroscopy and theoretical calculations reveal the true active sites and a synergistic effect among five elements, which endow us-HEA/C with significantly enhanced HER activity. The outstanding performance of us-HEA NPs on HER provide a potential application as sufficiently advanced catalysts in practical electrocatalytic hydrogen production.

Results

Synthesis and characterization of us-HEA NPs. Due to the vast difference in chemical and physical properties of mixing elements, the controllable synthesis of ultrafine HEA NPs without separate phases is quite difficult. In this work, a suitable and scalable synthetic strategy was achieved, which ensures the simultaneous reduction of the mixed metal salts (see Experimental section for details). After the co-reduction of five metal precursors and further annealing, single-phase NiCoFePtRh HEAs were ultimately obtained. The powder X-ray diffraction (PXRD) patterns (Supplementary Fig. 1) and energy dispersive spectroscopy (EDS) mapping (Supplementary Fig. 2) of the products provide direct evidence of the successful preparation of NiCoFePtRh HEAs. **The XRD patterns reveal that the NiCoFePtRh HEAs have a face-centered cubic (fcc) structure, similar to that of**

Fig. 1. Morphology, structure and composition characterization of ultrasmall NiCoFePtRh high-entropy alloy (us-HEA) nanoparticles (NPs). **a** Representative HAADF-STEM image and **b** the size distribution histogram of us-HEA NPs. **c** XRD pattern of us-HEA/C. **d** An enlarged HAADF-STEM image (inset shows the model of NPs growing on the carbon support) of us-HEA/C NPs. **e** Lattice spacing of a single NP marked in (d), showing only 8 atomic layers. HAADF-STEM image (f) of another single NP and the corresponding EDS elemental mapping of (g) Fe, (h) Ni, (i) Co, (j) Rh, and (k) Pt.

pure Pt. However, the sharp (111) peak at 43.2° implies a large crystal size, which was further verified by HAADF-STEM image in Supplementary Fig. 2. In order to prepare ultrasmall NPs with uniform dispersion, the carbon supports were added to the reaction solution prior to the co-reduction of metal salts²⁶ and a series of comparative samples with different loadings were obtained (Supplementary Fig. 3 and Fig. 4). Finally, 5 wt% loading in theory was determined to be the most appropriate in this work, labelled as us-HEA/C. Fig. 1a and Supplementary Fig. 5 illustrate the representative HAADF-STEM and TEM overview images of the 5 wt% us-HEA NPs loaded on the carbon support. The us-HEA NPs are uniformly dispersed on the carbon supports with an average diameter of 1.68 nm (Fig. 1b), which is much smaller than that of other reported HEAs (Supplementary Table 1). The XRD pattern (Fig. 1c) further confirms the ultrasmall crystal structure because no obvious diffraction peak is detected, which agrees with previous study on ultrasmall Pt nanocrystal²⁷. The enlarged HAADF-STEM image (Fig. 1d) implies a strong metal-support interaction. To verify this strong interaction,

the heat treatment temperature was increased to 550°C , conventionally cause particle coarsening, the particle size and diffraction peaks have no significant changes (Supplementary Fig. 6). Fig. 1e shows the high-resolution HAADF-STEM image of an us-HEA NP with only 8 atomic layers. The lattice spacing is $2.10\text{ \AA}$, which is corresponding to the (111) plane of XRD patterns (Supplementary Fig. 1 and Fig. 4), suggesting that us-HEA NPs have (111) basal planes and fcc structure. EDS mapping and line scanning profiles of a single us-HEA NP are shown in Fig. 1f-k and Supplementary Fig. 7a, respectively, revealing that all five elements are uniformly distributed and well-mixed without composition segregation. The atomic ratio of Ni:Co:Fe:Pt:Rh is 26.6:25.6:25.1:14.9:7.8 (Supplementary Fig. 7b), which is roughly in accordance with the overall composition analysis, measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Supplementary Table 2). It should be noted that long-time exposure under electron beams during the elemental mapping characterization would

Fig. 2. Characterization of atomic structure, electronic structure, and coordinational structure of us-HEA. **a** Atomically resolved HAADF-STEM image of an us-HEA NP. The corresponding Fourier filtered image (**b**), simulated crystal structure image (**c**), fast Fourier transformation (FFT) pattern (**d**), and simulated diffraction pattern (**e**) from the [011] zone axis of **a**. **f** X-ray absorption near edge structure (XANES) spectra for the Pt L_3 -edge. **g** XANES spectra for the Rh K-edge. **h** XANES spectra for the Ni K-edge. **i** XANES spectra for the Co K-edge. **j** The amount of electrons of the corresponding surface atom in pure metal and us-HEA (111) slab systems obtained from Bader charge analysis. The inset at the top is the two-dimensional charge density distributions of surface atoms in pure metals (Pt, Rh, Ni, Co, and Fe) and us-HEA (111) slab systems. The extended XAFS spectra for Pt L_3 -edge (**k**) and Rh K-edge (**l**). **m** An overlay of the extended XAFS spectra for all five x-ray probed elements in us-HEA/C.

electronegativity of these three metals resulting in the donation of electron density. Here it should be noted that the intensity variation of pre-edge and main features of these XANES at Fe, Co and Ni K-edge is due to the intrinsic size effect of the ultrasmall NPs as pointed by Rehr²⁸, rather than oxidation effect. The ab initio calculation simulated the XANES feature evolution with the size of nanoparticle (Supplementary Fig. 10 and 11). All the white lines are far away from the corresponding oxide reference sample, indicating that all the elements in the us-HEA NPs are in metallic states. The result of Bader charge analysis also confirms the transfer of electron density in the us-HEA (Fig. 2j). Overall, the above results indicate the redistribution of electrons and fine-tuning electronic structure of us-HEAs. While, any change to the electronic structure will influence the electrocatalytic activity of the catalyst. As shown in Supplementary Fig. 12, the transfer of electron density from neighbouring atoms to Pt atoms can effectively lower the Fermi level and the *d*-band centre position of Pt.

The extended XAFS (EXAFS) spectra were used to further determine the entire coordination structure of five metallic elements in the us-HEAs. Supplementary Fig. 13 shows the experimental k^2 -weighted EXAFS oscillations of us-HEA/C at Fe, Co, Ni, Rh K-edge and Pt L_3 -edge. The Fourier transforms (FT; No phase correction) of these EXAFS are displayed in Fig. 2k & 2l and Supplementary Fig. 14, compared with the FT-EXAFS the element metals and their oxides. The missing of the Me-O (Me: Fe, Co, Ni, Rh and Pt) shell (ca. 1.5 Å) for all FT curves of us-HEA/C means the as-prepared sample is not oxidized. The distance of all the first shells (Me-Me) in us-HEAs is shorter than that of their element metals, respectively, especially for the FT of Rh and Pt. Fig. 2m overlays all these FT curves for the first shell. The distance and amplitude are almost identical for the Fe, Co, and Ni absorbers, indicating these 3d transition metals have an identical local atomic structure and completely random mixing distribution in us-HEAs. For Rh and Pt, the distance is a little longer because of their larger atomic radii. Quantitative local structure was obtained by fitting all the FT-EXAFS spectra. The quality of fits is shown in Supplementary Fig. 15 and the fitted structural parameters summarized in Supplementary Table 3. The fitting results show the average coordination numbers (CN) of the first shells are almost the same for all probed metals, around 8.5. This CN value means the size of us-HEAs is ca. 1.5 nm, according to the “growth curve” of CN as function of nanoparticle size²⁹. The interatomic distances (R) between Fe, Co and Ni are identical, that is about 2.50 Å. The interatomic distance between Rh and Pt is about 3.85 Å. Hence the EXAFS quantitatively analysis suggests that these five metallic elements in us-HEAs form a solid-solution phase structure without elemental segregation.

Using the same synthesis method, eight other HEA NPs including PtRhAuIrPd, CoCuZnPtPd, NiCoCuPtAu, FeCoNiInPt, CoNiCdPtPdIr, NiCdPtPdIrAu, CoNiCdPtPdIrAu, and FeCoNiCuCdPtIrPd HEA NPs, have also been synthesized. The representative elemental maps of quinary (PtRhAuIrPd, CoCuZnPtPd, NiCoCuPtAu, and FeCoNiInPt), senary (CoNiCdPtPdIr and NiCdPtPdIrAu), septenary (CoNiCdPtPdIrAu), and octonary (FeCoNiCuCdPtIrPd) HEA NPs are shown in Supplementary Fig. 16. The elemental maps clearly reveal that each element in these HEAs is uniformly mixed without phase separation and provide direct evidence of alloy formation¹⁹.

Therefore, our synthesis method was strongly demonstrated as a general strategy for the synthesis of high-entropy alloy NPs.

Electrochemical performance of us-HEA NPs. The electrocatalytic HER activity of the us-HEA/C was investigated using a three-electrode setup in 0.5 M H₂SO₄ solution at room temperature. Several samples (including the commercial Pt/C, commercial Rh/C, Ketjen-black carbon (C), and precursors) were also measured under the same test conditions for comparison. Fig. 3a shows the specific activities normalized by geometric area without iR compensation. Although the noble metal loading of the us-HEA/C is only 0.8224 ug cm⁻², much lower than that of commercial Pt/C (32 ug_{Pt} cm⁻²) and other reported noble-metal catalysts (Supplementary Table 4), the us-HEA/C exhibits a smaller overpotential (27 mV) at the current density of 10 mA cm⁻². The us-HEA/C exhibits a Tafel slope of 30.1 mV dec⁻¹, also lower than that of commercial Pt/C (30.5 mV dec⁻¹), demonstrating the Volmer-Tafel mechanism as the HER pathway (Supplementary Fig. 17). The Nyquist plots indicate that us-HEA/C has a fast kinetics for HER (Supplementary Fig. 18). To characterize the intrinsic activity of these catalysts, the specific activities shown in Fig. 3b are all normalized to the electrochemically active surface area (ECSA) obtained by calculating the hydrogen absorption-desorption regions (Supplementary Fig. 19). As expected, the us-HEA/C exhibits the most favourable specific activities among all the catalysts, with the highest current density in the entire potential region. At a potential of -0.05 V (vs RHE), the us-HEA/C exhibits an ultrahigh specific activity (22.65 mA cm⁻²) (Fig. 3c), which is 19.0 and 29.1 times higher than that of the commercial Pt/C (1.19 mA cm⁻²) and Rh/C (0.78 mA cm⁻²), respectively.

Meanwhile, the mass activity of us-HEA/C also confirms its ultrahigh activity for HER. Supplementary Fig. 20 demonstrates that us-HEA/C has the optimal mass activity among the NiCoFePtRh HEA/C with different loadings in the entire potential region. Fig. 3d presents the LSV curves of several catalysts normalized by noble metal mass, indicating that the us-HEA/C catalyst has an absolute advantage. The mass activity of us-HEA/C is high up to 28.3 A mg⁻¹ at -0.05 V vs RHE (Fig. 3e), which is 40.4 and 74.5 times greater than those obtained from commercial Pt/C (0.70 A mg⁻¹) and Rh/C (0.38 A mg⁻¹), respectively. Even compared with those of other advanced noble metal catalysts reported in the recent literatures (Fig. 3f^{4,12,13,30-36} and Supplementary Table 5, the mass activity (28.3 A mg⁻¹) of us-HEA/C is the highest, proving that it is one of the best electrocatalysts for HER. These results suggest that the us-HEA can significantly increase the utilisation of noble metals and decrease the cost of the catalyst. To obtain a deeper insight into the intrinsic activities, the TOFs of the us-HEA/C and other reported catalysts are further investigated. As shown in Fig. 3g^{4,12,31,37-41} and Supplementary Table 5, the us-HEA/C demonstrates higher TOFs than those of other noble-metal catalysts at various overpotentials. In particular, the highest reported TOF of 30.1 s⁻¹ observed at 50 mV overpotential is 41.8 times higher than that of the Pt/C catalyst. The above results demonstrate that us-HEA/C has ultrahigh electrocatalytic activity for the HER, including outstanding specific activity, ultrahigh mass activity and TOF.

To evaluate the practicality of the catalyst, stability is another very important parameter, especially in acidic solutions. As shown in Fig.

3h, the accelerated degradation test (ADT) for 10,000 cycles between +0.1 and -0.2 V (vs RHE) at 100 mV s^{-1} , the polarization curve of the us-HEA/C catalyst does not exhibit any negative shift. In contrast, the polarization curves of both Pt/C and Rh/C have shown obvious deterioration after only 1000 cycles (Supplementary Figure 21). Moreover, after the 10,000 cycles test, the morphology of the us-HEA remains intact with no obvious particle growth and agglomeration (Supplementary Fig. 22). As a sharp contrast, commercial Pt/C catalyst agglomerates severely. The XRD pattern (Supplementary Fig. 23), elemental distributions (Supplementary Fig. 24), and lattice fringes (Supplementary Fig. 25) of us-HEA/C after stability test exhibit no noticeable change, indicating that the high-entropy nanocrystals have excellent structural stability. The line scanning profile (Supplementary Fig. 26) and EDS spectrum (Supplementary Fig. 27) of the us-HEA NPs collected after stability test evidence the superior compositional stability and corrosion

resistance. Fig. 3i shows a long-term stability test of the us-HEA/C for 100 h in the 0.5 M H_2SO_4 solution. After the harsh test for 85 h, us-HEA/C can maintain 100% of the initial current density (Supplementary Fig. 28). However, Pt/C and Rh/C only maintain 74.8% and 45.1% of the initial current densities, respectively (Supplementary Fig. 29). The above results fully demonstrate that the us-HEA NPs are remarkably stable. The excellent stability of the us-HEA/C can be attributed to the following reasons. First, the high-entropy stabilization effect, and high metallic element diffusion barriers. Second, the annealed us-HEAs have good crystallinity, preventing elemental segregation and etching. Third, tight bonding between the us-HEA NPs and carbon substrate prevents NPs agglomeration or segregation during the tests. Fourth, the us-HEA NPs were synthesized in acidic solutions, so non-noble metal components which are unstable or do not form alloys were already etched out in the synthesis process.

Fig. 4. Operando X-ray absorption near-edge structure (XANES) measurements and theoretical calculations of hydrogen-adsorption free energies (ΔG_{H^*}). **a** Schematic illustration of the operando electrochemical test of us-HEA catalyst during HER. In situ normalized XANES spectra of us-HEA/C recorded at different potentials in fluorescence mode at Rh K-edge (**b**), Fe K-edge (**c**), Ni K-edge (**d**), Co K-edge (**e**), and Pt $L_{3\text{-edge}}$ (**f**) (inset shows an enlarged view of the intensity). **g** Schematic illustration of the binding strength between H and the Rh site, Fe/Co/Ni site, and Pt site of us-HEA, respectively. **h** Calculated hydrogen-adsorption free energy (ΔG_{H^*}) profiles for three representative sites on us-HEA (111) surface and Pt site on pure Pt (111) surface at monolayer hydrogen coverage ($\theta_{\text{H}^*} = 1$).

In situ X-ray absorption near-edge structure (XANES) analysis. Precise identification of the operando catalytic sites and elucidation of the practical reaction process under the electrochemical operation conditions are urgently required. However, the aforementioned remains challenging because of the structural complexity of catalysts and the difficulty of exploration, particularly for complex multi-element systems (e.g., HEAs). Herein, we first employed in situ and operando X-ray absorption spectroscopy (XAS) to reveal the realistic reaction behaviours of HEAs, including the electronic state variation, identification of active sites, and parsing synergistic effect among the five elements. Fig. 4a and Supplementary Fig. 30 show the schematic diagram of electrochemical operando XAS measurements and digital photograph of the operando fluorescence cell, respectively. Prior to XAS measurements, the sample was activated and each potential was held for ~ 5 min to achieve a stable stage. The XANES spectra at Rh K-edge, Fe K-edge, Ni K-edge, Co K-edge, and Pt L₃-edge collected in fluorescence mode under the initial condition (immersed in H₂SO₄ solution) and different applied potentials are displayed in Fig. 4b-f. The XANES for all applied voltages keeps their dominant features unchanged, especially for the positions of the WL and the second nearest oscillations. It means the as-prepared HEA NPs stayed a high

stability in the reaction. When the cathodic potential of 0.05 V vs RHE (no HER occurs) was applied, the absorption edge of Rh dramatically shifted to a lower energy compared to the initial state, indicating that Rh gained numerous electrons and a large number of hydrogen ions were adsorbed on the surface of Rh sites. In contrast, the absorption edges of the other four elements changed a little. This is because hydrogen has a stronger adsorption binding strength at fcc sites with Rh nearby (Rh site) than those at fcc sites with only Fe/Co/Ni nearby (Fe/Co/Ni site) and at fcc sites with Pt nearby (Pt site) on the us-HEA (111) surface (Fig. 4g). Hence, hydrogen ions prefer to adsorb on Rh sites and Rh site contributes greatly to the Volmer step in HER. The hydrogen adsorption on Rh site can also be confirmed by the intensity decrease of the peak at about 23260 eV versus the main peak (Supplementary Fig. 31 and Table 6)⁴². With the increase in the applied potential to -0.01 V and -0.05 V, the XANES spectra of Fe, Ni, and Co do not shift any further, but also do not return to the original state (Supplementary Fig. 32), thus indicating that a small percentage of the Fe/Co/Ni sites participate in HER. While the Rh XANES edge continues to shift slightly to lower energy, suggesting that the number of hydrogen ions adsorbed on the surface of Rh sites increases and HER occurs directly on the Rh sites. Notably, the WL of the Pt XANES edge declines sharply when HER begins (-0.01 V), which

Fig. 5. Tafel activation barriers from theoretical calculations. Free energy diagrams of the Tafel reaction based on fcc-fcc (a-d), top-fcc (e-h), and top-top (i-l) model on Pt (111) (a, e, i) and us-HEA (111) (b-d, f-h, j-l) surface. a-d Tafel reaction barrier on the Pt (111) surface for fcc_{Pt}-fcc_{Pt} model (a) and us-HEA (111) surface for fcc_{Pt}-fcc_{Pt} model (b), desorption of H* at fcc_{Rh} (c) and fcc_{Fe/Co/Ni} (d) site after migration. e-h Tafel reaction barrier on the Pt (111) surface for top_{Pt}-fcc_{Pt} model (e) and us-HEA (111) surface for top_{Pt}-fcc_{Pt} model (f), desorption of H* at top_{Rh} (g) and top_{Fe/Co/Ni} (h) site after migration. i-l Tafel reaction barrier on the Pt (111) surface for top_{Pt}-top_{Pt} model (i) and us-HEA (111) surface for top_{Pt}-top_{Fe/Co/Ni} model (j), desorption of H* at top_{Rh} (k) and top_{Fe/Co/Ni} (l) site after migration. The inset shows the corresponding optimized adsorption structures for the initial state, the transition state (TS), and the final state.

amply illustrates that Pt sites are the main active sites for HER at this moment. The valence state of Rh and Pt with function of the edge position and the WL intensity, respectively, was plotted in Supplementary Fig. 33. The above operando XAS results show that both Rh and Pt are the main and direct active sites, which boost HER together.

Density functional theory (DFT) calculations. Hydrogen-adsorption free energy (ΔG_{H^*}) is a widely used and reasonable descriptor for the ability of HER^{12,35,39}. Fig. 4h and Supplementary Table 7 shows the specifically calculated ΔG_{H^*} of HER for three types of representative sites (Supplementary Fig. 34) at monolayer hydrogen coverage ($\theta_{H^*} = 1$) on us-HEA (111) surface and Pt site on pure Pt (111) surface. The Pt site in the us-HEA has the smallest absolute ΔG_{H^*} (-0.004 eV) among the three types of representative sites on the us-HEA (111) surface, and is smaller than that in pure Pt (-0.070 eV). The smaller absolute ΔG_{H^*} in us-HEA (111) surface was confirmed within three other structural models (Supplementary Fig. 35 and 36). **The modified electronic structure of Pt in the us-HEA enables the Pt site to achieve an optimum Pt-H binding value, which might lead to a rapid H⁺ adsorption and H₂ release process, ultimately accelerating HER.**

But only the ΔG_{H^*} descriptor cannot be representative for the HER activity. Peterson and coworkers have raised the concern on the challenge to the $\Delta G_{H^*} \sim 0$ interpretation of hydrogen evolution⁴³. Therefore, to further reveal the origin of the superior intrinsic activity and thoroughly elucidate the catalytic mechanism of us-HEA, we systematically studied the kinetic aspect in terms of the activation barrier of the rate limiting step, Tafel reaction. Three reaction models including fcc-fcc (desorption of two H⁺ at fcc sites), top-fcc (desorption of one H⁺ at top site and another H⁺ at fcc site), and top-top (desorption of two H⁺ at top sites) model were investigated. Based on fcc-fcc model at $\theta_{H^*} = 1$, the activation barrier for the Tafel step ($\Delta G_T^\ddagger$) on the Pt (111) surface is 0.831 eV (Fig. 5a), which is consistent with that of 0.80~0.95 eV in Norskov's work⁴⁴ and Peterson's work⁴³. For the desorption of H⁺ at Pt site (fcc_{Pt} site) on the us-HEA (111) surface, the $\Delta G_T^\ddagger$ based on fcc_{Pt}-fcc_{Pt} model is 0.756 eV (Fig. 5b), which is considerably lower than that of Pt (111) surface, indicating an faster desorption for two H⁺ at fcc_{Pt} site on us-HEA (111) surface. The $\Delta G_T^\ddagger$ based on fcc_{Rh}-fcc_{Rh} model is 0.884 eV (Supplementary Fig. 37a), which is higher than that of fcc_{Pt}-fcc_{Pt} model. However, we identified two easier alternative desorption routes for H⁺ at fcc_{Rh} site. The first route is that the H⁺ at fcc_{Rh} site desorbs with the H⁺ at the neighbouring fcc_{Pt} site (fcc_{Rh}-fcc_{Pt} model), which shows a $\Delta G_T^\ddagger$ of 0.796 eV (Supplementary Fig. 37b), lower than that of fcc_{Rh}-fcc_{Rh} model, even easier than that of fcc-fcc model on the Pt (111) surface. The second route is that the H⁺ at fcc_{Rh} site migrates to fcc_{Pt} site before desorption ($\theta_{H^*} = \frac{15}{16}$). The activation barrier for H⁺ migration is as low as ~0.33 eV, followed by a desorption of two H⁺ at fcc_{Pt} sites with a relatively low activation barrier of 0.651 eV (Fig. 5c). This indicates that the desorption of H⁺ at the fcc_{Rh} site on us-HEA (111) surface could be easier than that of H⁺ at the fcc_{Pt} site on Pt (111) surface. Similarly, we also analyzed the Tafel steps for H⁺ at fcc_{Fe/Co/Ni} sites (Fig. 5d and Supplementary Fig. 37c, d) and determined that they are similar to those H⁺ at fcc_{Rh} sites. The Tafel activation barriers of both the desorption of H⁺ at fcc_{Fe/Co/Ni}

site with the H⁺ at the neighbouring fcc_{Pt} site (fcc_{Fe/Co/Ni}-fcc_{Pt} model) and the desorption of H⁺ at fcc_{Fe/Co/Ni} site assisted by H⁺ migration from fcc_{Fe/Co/Ni} to fcc_{Pt} site are lower than that on the Pt (111) surface. Hence, the desorption of H⁺ at the fcc_{Pt}, fcc_{Rh}, and fcc_{Fe/Co/Ni} sites on the us-HEA (111) surface could be all easier than that on the Pt (111) surface based on fcc-fcc model.

Furthermore, based on top-fcc model at $\theta_{H^*} = \frac{17}{16}$, $\Delta G_T^\ddagger$ on the Pt (111) surface is 0.511 eV (Fig. 5e), which is consistent with previous works^{43,45}. As for us-HEA (111) surface, the activation barrier for the desorption of one H⁺ at Pt top site (top_{Pt} site) and another H⁺ at fcc_{Pt} site (top_{Pt}-fcc_{Pt} model) is only 0.238 eV (Fig. 5f). The $\Delta G_T^\ddagger$ for top_{Rh}-fcc_{Rh} model (Supplementary Fig. 38a) and desorption of H⁺ at top_{Rh} after H⁺ migration from top_{Rh} to top_{Pt} (Fig. 5g) on us-HEA (111) surface indicates that the desorption of H⁺ at top_{Rh} site could be easier than that of top-fcc model on Pt (111) surface. The desorption for H⁺ at top_{Fe/Co/Ni} sites on us-HEA (111) after H⁺ migration from top_{Fe/Co/Ni} to top_{Pt} site also show lower $\Delta G_T^\ddagger$ than that on Pt (111) surface based on top-fcc model (Fig. 5h and Supplementary Fig. 38b). Thus, the Tafel reaction activity of H⁺ at top_{Pt}, top_{Rh}, and top_{Fe/Co/Ni} sites on us-HEA (111) surface could be superior to that on the Pt (111) surface based on top-fcc model. In addition, as shown in Fig. 5i-l and Supplementary Fig. 39, the H⁺ at top_{Pt}, top_{Rh}, and top_{Fe/Co/Ni} sites on us-HEA (111) surface would show faster desorption than that on the Pt (111) surface based on top-top model at $\theta_{H^*} = \frac{18}{16}$. In brief, $\Delta G_T^\ddagger$ on us-HEA (111) surface are lower than that on Pt (111) surface, regardless of fcc-fcc, top-fcc, and top-top models. **Moreover, we have simulated the macroscopic observables in terms of potential-dependent current densities, Tafel slopes and coverages of the fcc-fcc, top-fcc, and top-top mechanisms (Supplementary Fig. 40), also confirming the better HER activity of us-HEA (111) surface.**

The calculations above reveal that the five elements in the us-HEA show a synergistic effect in Volme-Tafel mechanism, enabled by the modified electronic structure. Pt sites on us-HEA (111) surface show excellent activity in Tafel step, while Rh and Fe/Co/Ni sites need the assistant of Pt site in Tafel step. The Rh element play an important role in Volmer step as the hydrogen adsorption energy is relatively low. Therefore, Pt and Rh elements are the main and direct active sites of us-HEA toward hydrogen evolution, verifying the operando XAS results.

Based on the discussion above, the origin of the ultrahigh hydrogen evolution activity of us-HEAs can be explained as follows. First, the us-HEA has ultrasmall nanoparticles and ultrahigh atom utilization. Second, there is a synergistic effect among the five atoms, which is also confirmed by experiments (Supplementary Fig. 41). **Third, the us-HEA demonstrates tunable electronic structures, contributing the optimum hydrogen-adsorption free energies and low activation barriers.** All of the aforementioned characteristics will intrinsically contribute to the superior electrocatalytic activity of ultrasmall NiCoFePtRh HEA NPs toward hydrogen evolution.

Conclusions

In summary, we demonstrated the extremely superior performance and stability of novel NiCoFePtRh us-HEA NPs as an advanced and practical electrocatalyst in acidic media. The use of an ultrafast and

powerful chemical co-reduction method leads to the formation of uniform HEA nanocrystals with the smallest reported particle size (~1.68 nm). XAFS measurements demonstrate fine-tuning of the electronic structure of us-HEA. As an electrocatalyst for HER, us-HEA/C achieves an ultrahigh mass activity of 28.3 A mg⁻¹_{noble metals} at -0.05 V, which is 40.4 and 74.5 times higher than those of the commercial Pt/C and Rh/C catalysts, respectively. Moreover, the us-HEA/C exhibits the highest reported TOF (30.1 s⁻¹) at 50 mV overpotential (41.8 times higher than that of the Pt/C catalyst) and excellent stability with no decay after 10,000 cycles. Both operando X-ray absorption spectroscopy and theoretical calculations reveal the actual active sites and a synergistic effect among the five elements, which endow us-HEA with significantly enhanced HER activity. The extraordinarily high performance of the supported us-HEA NPs provides a potential application as a sufficiently advanced HER catalyst for the storage of future renewable energy.

Methods

Synthesis of us-HEA Nanoparticles

Ultrasmall NiCoFePtRh HEA NPs were synthesized by the co-reduction of five metal salts under argon-filled conditions, followed by annealing. Using a typical procedure, FeSO₄·7H₂O (0.02 mmol), NiSO₄·6H₂O (0.02 mmol), CoSO₄·7H₂O (0.02 mmol), Rh₂(SO₄)₃·4H₂O (0.005 mmol), and H₂PtCl₆·6H₂O (0.01 mmol) were dissolved in 0.002 M H₂SO₄ solution (50 mL) in an argon-filled box, and stirred to form a clear solution. Then, Ketjen-black carbon powders (122.7 mg) were added to the clear solution, and the mixture was stirred continuously to form a uniformly dispersed solution. Next, the saturated aqueous solution of sodium borohydride was added to the above solution under vigorous stirring for 8 h. Finally, the sample was separated from the mixture via centrifugation. The sample was then washed with argon-saturated ultrapure water and ethanol solution, and dried at 70 °C for 6 h in a glovebox. The obtained precursors were quickly transferred to a tube furnace and treated under flowing H₂/Ar at 350 °C for 3 h. The obtained us-HEA/C NPs (5 wt%) were finally stored in a glovebox under Ar for further characterization and electrochemical measurements. The synthesis of eight other HEAs with different compositions and NiCoFePtRh HEA/C with other loadings followed the similar procedure to that of us-HEA/C NPs.

Material Characterizations

XRD patterns were collected on an X-ray diffractometer (Bruker D8, Cu K_α, λ = 1.5406 Å, 40 kV, and 40 mA) with a counting time of 8 s, and recorded with 2θ ranging from 10° to 80°. The morphologies and composition of the samples were characterized by high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, 200 kV) equipped with an EDS instrument. The atomic structural characterization of the samples was determined using an aberration-corrected FEI Titan Cubed Themis G2 microscope operated at 300 kV equipped with an X-FEG gun and Bruker Super-X EDX detectors. The beam current was ~50 pA, the convergence semiangle was 30 mrad, and a collection semi-angle snap was 80-379 mrad. The STEM-EDX mapping are acquired at a beam current of ~50 pA and counts ranging from 1k cps to 3k cps for ~15 min with a Bruker Super-X EDS four-detector. Due to the ultrasmall nanostructure, the electron exposures used should be very low to minimize irradiation damage

during the TEM measurements. The XAFS spectra of the us-HEA at the Pt L₃-edge, Ni K-edge, Co K-edge, and Fe K-edge were collected at beamline 1W1B of the Beijing Synchrotron Radiation Facility, and that at the Rh K-edge was collected at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility. It should be noted that the samples were kept under an argon atmosphere before all the above characterizations to avoid oxidation.

Electrochemical Measurements

All the electrochemical measurements of the HER were performed in a standard three-electrode electrochemical cell using a BioLogic SP 240 electrochemical workstation. The glassy carbon (GC) film and mercury/mercurous sulphate electrode (Hg/HgSO₄) were used as the counter and reference electrodes, respectively. The working electrode was prepared as follows: 2 mg of us-HEA/C sample was dispersed in 1 mL of isopropyl alcohol, ultrapure water, and 5% Nafion mixture solution. The mixture was then transferred to an ultrasonic bath to form a homogeneous catalyst ink. A 10 μL aliquot of the obtained suspension was pipetted onto the GC rotating disk electrode and dried naturally for the electrochemical measurements. The loading of noble metals (Pt and Rh) in us-HEA is 0.8224 μg cm⁻². The working electrode fabrication procedures of Pt/C (20 wt%) and Rh/C (5 wt%) were the same for the us-HEA/C sample. The HER tests were conducted in N₂-saturated 0.5 M H₂SO₄ solution at a rotation rate of 2000 rpm.

TOF is defined as the number of H₂ evolved on an active site per second¹². In us-HEA/C, only a small percentage of Fe/Co/Ni near the Pt sites participates in HER and must depend on the help of Pt to complete the reaction. So, Pt is the true active site, and the H₂ evolves mainly on Pt active site. Rh site contributes greatly to the first step (Volmer step) of HER reaction due to strong adsorption strength with hydrogen. The Fe/Co/Ni atoms mainly play a role of effectively adjusting the electronic structures of Pt/Rh atoms and increasing the entropy of the us-HEAs to improve the stability. In brief, Rh and Pt are the main and direct active sites, mainly contributing to HER. Therefore, we calculated the mass activity and TOFs of the us-HEA/C mainly based on Pt and Rh sites. The TOF is calculated by the following equations^{4,12}:

$$\text{TOF} = \frac{\text{Total number of hydrogen turnover}_{\text{geometric}} \cdot \text{area}}{\text{Number of active sites}_{\text{geometric}} \cdot \text{area}}$$

$$\text{Total number of hydrogen turnover} = (|j| \text{ mA cm}^{-2}) \left(\frac{1 \text{ C s}^{-1}}{1000 \text{ mA}} \right) \left(\frac{1 \text{ mol e}^{-}}{96485.3 \text{ C}} \right) \left(\frac{1 \text{ mol}}{2 \text{ mol e}^{-}} \right) \left(\frac{6.022 \times 10^{23} \text{ molecules H}_2}{1 \text{ mol H}_2} \right) = 3.12 \times 10^{15} |j| \text{ H}_2 \text{ s}^{-1} \text{ cm}^{-2} \text{ per mA cm}^{-2}$$

$$\text{Number of active sites (noble metal)} = \left(\frac{\text{Catalyst loading on the electrode (g cm}^{-2}\text{)} \times \text{noble metal content (wt\%)}}{\text{noble metal atomic weight (g mol}^{-1}\text{)}} \right) \times 6.022 \times 10^{23} \text{ sites mol}^{-1}$$

$$\text{TOF} = \frac{3.12 \times 10^{15}}{\text{Number of active sites}} \times |j|$$

Operando XAS Measurements

The operando XANES spectra of the us-HEA at the Pt L₃-edge, Ni K-edge, Co K-edge, and Fe K-edge were also collected at beamline 1W1B of the Beijing Synchrotron Radiation Facility in fluorescence mode, and Rh K-edge was collected at beamline BL14W1. The operando fluorescence cell was designed by Beijing Scistar Technology Co Ltd. The electrochemical measurements of the HER were conducted at room temperature using a CHI 760E electrochemical workstation. A carbon rod, Hg/HgSO₄, and us-HEA/C-coated carbon paper were used as the counter electrode, reference electrode, and working electrode, respectively. 0.5 M H₂SO₄ solution was added to the operando fluorescence cell by a peristaltic pump.

Computational Methods

All the DFT calculations in this work were performed using the Vienna Ab-initio Simulation Package (VASP)^{46,47} with Perdew-Burk-Ernzerhof (PBE) functional⁴⁸. The planewave basis with a cutoff energy of 520 eV and projector-augmented wave (PAW) pseudopotential were used. The atomic positions were completely optimized until the Hellmann-Feynman force was less than 0.01 eV/Å and the total energy convergence criterion was set to 1×10^{-5} eV. The Pt (111) and us-HEA (111) surfaces were modelled by a symmetric periodic slab with a vacuum layer separation larger than 14 Å to avoid interlayer interactions. A 4×4 super cell with seven atomic layers containing 112 atoms was used. The Pt and Rh atoms are uniformly distributed, and Fe/Co/Ni atoms are randomly distributed in us-HEA (111) slab model, as EXAFS fitting results indicate that Fe/Co/Ni atoms have a completely random mixing distribution in us-HEAs, while Pt and Rh atoms are highly dispersed among the Fe-Co-Ni solid solution. The Monkhorst-Pack⁴⁹ k-point grid $3 \times 3 \times 1$ was set in all calculations. The calculation of the Gibbs free energy of the intermediates followed the Nørskov method⁵⁰.

The Gibbs free energy (ΔG) is defined as follows: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the change of electronic energy obtained from DFT calculations, ΔZPE is the change of zero-point energy, and ΔS is the entropy difference. The contribution of vibration of all adsorbed species was considered in our calculation. We selected two adjacent fcc site to investigate the reaction barrier of the Tafel pathway. The adsorptions of two hydrogen atoms and the hydrogen molecule were taken as initial state and final state of the Tafel pathway ($H^* + H^* = H_2$). The transition state of the reaction was obtained by the climbing image nudged elastic band (CI-NEB) method⁵¹, then confirmed by vibrational frequency analysis. The Tafel activation energies ($\Delta G_T^\ddagger$) were calculated by $(\Delta G_T^\ddagger) = G_{TS} - G_{ini}$ ($G = E_{DFT} + ZPE - TS$) where G_{TS} and G_{ini} are the free energies of the transition and initial states of hydrogen adsorption on the substrate.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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Acknowledgments

This work was financially supported by the National Key R & D Program of China (No. 2016YFB0100200), the National Natural Science Foundation of China (No. 51671004 and U1764255), China Postdoctoral Science Foundation (2020T130004), and the Beijing Municipal Natural Science Foundation (No. 2181001). The first-principles calculations were supported by High-performance Computing Platform of Peking University. All support for our work is gratefully acknowledged.

Author Contributions

G. F. and D. X. conceived the idea. G. F. carried out the sample synthesis, characterization and performance measurement. F. N., G. F., and D. X. performed the DFT simulation and theoretical analyses. H. S., K. Z., and J. S. helped with the XAFS measurements. W.C. and G. F. performed the XAFS fits and analyses. Z. D. and P. G. helped with the HAADF-STEM measurements and discussion. The manuscript was written by G. F. and D.X. W.C. and D.X. edited the manuscript. All authors contributed to discussing and revising the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

Morphology, structure and composition characterization of ultrasmall NiCoFePtRh high-entropy alloy (us-HEA) nanoparticles (NPs). a Representative HAADF-STEM image and b the size distribution histogram of us-HEA NPs. c XRD pattern of us-HEA/C. d An enlarged HAADF-STEM image (inset shows the model of NPs growing on the carbon support) of us-HEA/C NPs. e Lattice spacing of a single NP marked in (d), showing only 8 atomic layers. HAADF-STEM image (f) of another single NP and the corresponding EDS elemental mapping of (g) Fe, (h) Ni, (i) Co, (j) Rh, and (k) Pt.

Figure 2

Characterization of atomic structure, electronic structure, and coordinational structure of us-HEA. a Atomically resolved HAADF-STEM image of an us-HEA NP. The corresponding Fourier filtered image (b), simulated crystal structure image (c), fast Fourier transformation (FFT) pattern (d), and simulated diffraction pattern (e) from the [011] zone axis of a. f X-ray absorption near edge structure (XANES) spectra for the Pt L₃-edge. g XANES spectra for the Rh K-edge. h XANES spectra for the Ni K-edge. i XANES spectra for the Co K-edge. j The amount of electrons of the corresponding surface atom in pure metal and us-HEA (111) slab systems obtained from Bader charge analysis. The inset at the top is the two-dimensional charge density distributions of surface atoms in pure metals (Pt, Rh, Ni, Co, and Fe) and us-HEA (111) slab systems. The extended XAFS spectra for Pt L₃-edge (k) and Rh k-edge (l). m An overlay of the extended XAFS spectra for all five x-ray probed elements in us-HEA/C.

Figure 3

Electrocatalytic performance of us-HEA/C electrocatalyst for hydrogen evolution reaction (HER) in 0.5 M H₂SO₄ solution. a HER polarization curves of us-HEA/C, the precursor, C, commercial Rh/C, and commercial Pt/C, normalized by geometric area. b ECSA normalized HER polarization curves of us-HEA/C, the precursor, C, commercial Rh/C, and commercial Pt/C. c Quantitative comparisons of the specific activities normalized by ECSA of us-HEA/C, commercial Rh/C, and commercial Pt/C at different potentials. d Noble-metal mass loading normalized HER polarization curves of us-HEA/C, the precursor, C, commercial Rh/C, and commercial Pt/C. e Quantitative comparisons of the mass activities of us-HEA/C, commercial Rh/C, and commercial Pt/C at different potentials. f Mass activity comparisons of us-HEA/C at -0.05 V versus RHE with state-of-the-art noble metal catalysts reported in recent literatures. g Turnover frequency (TOF) comparisons of us-HEA/C with other advanced noble metal catalysts reported

previously. Stability tests of us-HEA/C through potential cycling 10,000 cycles, normalized by geometric area (h) and constant applied potential for 100 h (i). All the results were not iR corrected.

Figure 4

Operando X-ray absorption near-edge structure (XANES) measurements and theoretical calculations of hydrogen-adsorption free energies (ΔG_{H^*}). a Schematic illustration of the operando electrochemical test of us-HEA catalyst during HER. In situ normalized XANES spectra of us-HEA/C recorded at different potentials in fluorescence mode at Rh K-edge (b), Fe K-edge (c), Ni K-edge (d), Co K-edge (e), and Pt L_3 -edge (f) (inset shows an enlarged view of the intensity). g Schematic illustration of the bonding strength between H and the Rh site, Fe/Co/Ni site, and Pt site of us-HEA, respectively. h Calculated hydrogen-

adsorption free energy (ΔG_{H^*}) profiles for three representative sites on us-HEA (111) surface and Pt site on pure Pt (111) surface at monolayer hydrogen coverage ($\theta_{H^*} = 1$).

Figure 5

Tafel activation barriers from theoretical calculations. Free energy diagrams of the Tafel reaction based on fcc-fcc (a-d), top-fcc (e-h), and top-top (i-l) model on Pt (111) (a, e, i) and us-HEA (111) (b-d, f-h, j-l) surface. a-d Tafel reaction barrier on the Pt (111) surface for fccPt-fccPt model (a) and us-HEA (111) surface for fccPt-fccPt model (b), desorption of H^* at fccRh (c) and fccFe/Co/Ni (d) site after migration. e-h Tafel reaction barrier on the Pt (111) surface for topPt-fccPt model (e) and us-HEA (111) surface for topPt-fccPt model (f), desorption of H^* at topRh (g) and topFe/Co/Ni (h) site after migration. i-l Tafel reaction barrier on the Pt (111) surface for topPt-topPt model (i) and us-HEA (111) surface for topPt-topFe/Co/Ni model (j), desorption of H^* at topRh (k) and topFe/Co/Ni (l) site after migration. The inset shows the corresponding optimized adsorption structures for the initial state, the transition state (TS), and the final state.

Supplementary Files

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