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Full Length Article

Unveiling the heterogeneous structure of FeCoNiPdCu High-Entropy Alloy: A case study on electrochemical nitrate reduction

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ABSTRACT

Recently, high-entropy nanoalloys (HEA) had attracted significant interest in various potential catalytic applications due to their unique high-entropy effect. However, in most previous studies, the successful preparation of single-phase HEA has been identified primarily through X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry, often neglecting the presence of minor secondary phases owing to the spatially averaged information provided by XRD. In this work, using FeCoNiPdCu HEA applied to an electrochemical nitrate reduction reaction (NO₃RR) as an example, we confirmed that trace amounts of oxygen induced the formation of a FeCoNiPdCu high-entropy oxide/FeCo oxide@NiPdCu alloy/FeCoNiPdCu HEA three-layer heterogeneous structure, achieving a Faradaic efficiency of 95.16% at an applied potential of -0.7 V vs. RHE. Moreover, by modifying the oxygen content, the element distribution across the entire HEA can be tuned owing to differences in oxide formation enthalpy, further affecting catalytic activity and selectivity. Our work deepens the understanding of HEA structures and provides insights into the active sites and corresponding catalytic mechanisms.

1. Introduction

Recently, high-entropy nanoalloys (HEA), composed of five or more elements in near equimolar ratio, had attracted significant interest due to the unique high-entropy effect [1–4], as well as their potential applications in various fields, such as electrocatalysis [5–10], photocatalysis [11–13], and thermocatalysis [14,15]. Among these applications, electrocatalytic nitrate reduction (NO₃RR) has gained significant attention as a sustainable alternative pathway for ambientcondition ammonia synthesis [16]. In addition, the NO₃RR approach simultaneously addresses environmental remediation challenges, as nitrate represents a ubiquitous nitrogen-containing pollutant in industrial effluents [17]. Integrating value-added ammonia production with industrial wastewater treatment under mild conditions established electrocatalytic nitrate-to-ammonia conversion as a dual-purpose strategy with economic and environmental benefits. The first HEA electrocatalyst for NO₃RR was designed by Zhi's group; their fabricated nanostructured FeCoNiAlTi alloy with a unique multi-element synergistic effect exhibited enhanced Faradaic efficiency compared with the bulk highentropy alloy [18]. Very recently, Ho's group demonstrated that a broad adsorption energy landscape in the single-phase HEA results in an excellent NO₃RR performance, with a high Faradaic efficiency of 94.5% [19]. Despite substantial advancements in preparing highly efficient and stable HEA [1,10,20,21], establishing an accurate relationship between catalytic performance and structure remains a significant challenge due to the wide variety of active sites and their random distribution.

Moreover, due to the high surface energy of nanomaterials, certain nano-alloys are prone to oxidation, forming ultrathin oxide layers on their surfaces when exposed to air. It was demonstrated by Liu's group that a thin FeCoNiCuSn oxide layer can spontaneously form on FeCo-NiCuSn nanoparticles, and the synergistic effects between the oxide layer and the nanoparticles provided excellent supercapacitive performance [22]. In catalytic reactions involving surface chemistry, the thickness of the active layer on the catalyst surface is typically around

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20 nm [23]. Thus, the presence of an oxide layer can critically impact catalytic activity. However, detailed research on the formation mechanism and properties of the oxide layer on HEA' surfaces remains scarce, which is crucial for identifying the active sites and analyzing the catalytic mechanism.

In our work, using FeCoNiPdCu HEA applied to NO₃RR as an example, three FeCoNiPdCu-based HEA samples were prepared by adjusting surface oxide layer characteristics with an oxygen passivation technique, thereby establishing the relationship between surface structure and catalytic performance. The experimental results demonstrate that oxygen induces the formation of a FeCoNiPdCu high-entropy oxide/FeCo oxide@NiPdCu alloy/FeCoNiPdCu HEA three-layer heterogeneous structure. Furthermore, by modifying the oxygen content, the element distribution across the entire HEA can be tuned based on differences in oxide formation enthalpies. Compared to the HEA with oxygen passivation treatment, the pristine HEA sample exhibits a higher NO₃RR activity and selectivity, achieving a Faradaic efficiency of 95.16% at a potential of -0.7 V vs. RHE. Our work is crucial for establishing a theoretical model structure for HEA and analyzing the active sites and corresponding catalytic mechanisms.

2. Results and discussion

In this study, metal ion precursors were anchored with chitosan and precipitated with NaOH solution, with the final products collected after heat treatment. The difference between obtained three HEA-based products was determined by their passivating process [24–26], including natural cooling (HEA-0), the flow rate of O₂/Ar mixture gas is 10 sccm (HEA-10) and 50 sccm (HEA-50) (detailed preparation process was shown in Experimental Section). The X-ray diffraction (XRD) results

demonstrated that all the prepared samples exhibited a single-phase solid-state structure, which was consistent with that of Cu@C (JCPDS No. 04-0836) (Fig. 1a). Furthermore, the peak positions and half-peak widths remained unaltered. Subsequently, the inductively coupled plasma optical emission spectrometer (ICP-OES) in Fig. 1b demonstrated that each metal atom's ratio in these samples was consistent, ranging from 5% to 35%. Notably, the significant differences in atomic radius and electronegativity between the Pd element and Fe, Co, Ni, and Cu elements resulted in considerable elemental fluctuations and gradients while preparing the obtained FeCoNiPdCu HEA [27]. Usually, combined with the XRD pattern and ICP-OES results, the successful preparation of high entropy nanoalloy could be confirmed. However, it was important to note that the XRD technique might potentially lead to the erroneous identification of an alloy as a single-phase solid solution because the fact that it only provided spatially averaged information and was unable to detect the presence of minor amounts of secondary phases [28,29]. Scanning electron microscopy (SEM) revealed the formation of FeCo-NiPdCu HEA with an approximate diameter of 100 nm on the catalyst surface (Fig. 1c). Moreover, the high-resolution transmission electron microscopy (HRTEM) image showed that the lattice spacing of 0.21 nm corresponding to the (111) plane (Fig. 1d). It should be noticed that an amorphous layer was observed on the HEA-0 surface. In contrast, crystallinity changes on the surface of HEA-10 catalysts were less pronounced (Supporting Information Fig. S1). Zhou's group employed in situ HRTEM technique to investigate the surface oxygen passivation mechanism [30], their results revealed that the surface passivation occurs via a two-stage process starting with the intralayer atomic disordering upon the incorporation of oxygen into both surface and subsurface regions of the metal lattice, followed by interlayer disordering that leads to full amorphization of the oxide layer. This



Fig. 1. (a) The XRD pattern of Cu@C, HEA-0, HEA-10, and HEA-50. (b) ICP-OES characterization of HEA-0, HEA-10 and HEA-50. (c) SEM image and particle size distribution of HEA-0. (d) HRTEM image of HEA-0. (e-i) The element mapping of HEA-0.

observation demonstrated that HEA-0 exhibited a higher degree of oxidation than other samples. However, due to the structural complexity of the HEA-based material, the accurate physical characteristic information (such as atomic composition and crystal structure) cannot be exclusively determined from the HRTEM image. Elemental mapping presents the uniform distribution of Cu, Co, Pd, Ni, and Fe on the HEA-0 (Fig. 1e-i).

To gain further insight into the structure of prepared samples, electrochemical NO3RR was performed in 14000 ppm KNO3-N and 0.5 M Na₂SO₄ electrolyte. Before the test, the standard concentration calibration curves for the NH₄⁺, NO₃⁻, and NO₂⁻ were collected (Supporting Information Fig. S2-S4). The linear sweep voltammetry (LSV) results demonstrated that HEA-10 exhibited the highest current density among these samples, suggesting that oxygen passivation treatment exerted a considerable influence on the electronic structure of the catalyst surface (Fig. 2a). Further analysis of the Faradaic efficiency (FE) results in Fig. 2b revealed that the order of FE (NH $_4^+$) was HEA-0 > HEA-50 > HEA-10 > Cu, with HEA-0 reaching a maximum of 95.16% at -0.7 V vs. RHE (Supporting Information Fig. S5 and S6). In addition, the concentration evolution of NH_4^+ , NO_3^- , and NO_2^- is systematically presented in Fig. S7. Notably, HEA-0 demonstrated a superior NO₃RR performance compared to HEA-10. When the working potential was -0.7 V vs. RHE, the NO_3^- concentration quickly decreased to 0.76 mol L⁻¹ (HEA-0), while for the HEA-10, only 0.80 mol L^{-1} of NO₃ was reduced to NO₂ and NH₄⁺. A comparison of HEA-0 with some other recent nitrate-reducing materials is shown in Table S1. Significantly, the Faradaic efficiency of the HEA-10 sample gradually decreases after 4 cycles. In comparison, the HEA-0 catalyst maintains more than 90% FE after 6 cycles, indicating HEA-0 demonstrated superior electrochemical durability relative to HEA-10 under identical operational conditions (Fig. S8). In addition, the prepared HEA-0 samples exhibited superior activity and selectivity compared to the original Cu samples, demonstrating that the unique cocktail effect of high-entropy materials can significantly improve the catalytic performance of NO3RR (ammonia-producing sub-current and ammonia-producing yield rate were shown in the Fig. 2c-d). To verify the elemental origin of ammonium radicals generated during nitrate reduction, we conducted ¹⁵N isotopic labeling experiments on nitrate, both labeled and unlabeled post-reaction solutions via ¹H NMR spectroscopy. Under acidic conditions, ¹⁵NH₃ and ¹⁴NH₃ exhibited distinct doublet and triplet splitting patterns, respectively. Only the ¹⁵NH₃ signal was observed in the isotope-labeled group, confirming that nitrate in the solution served as the sole nitrogen source during NH₃ formation (Supporting Information Fig. S9). Similarly, the selectivity of hydrogen and nitrite was also tested, and the results revealed that the hydrogen and nitrite FE of Cu was the largest within the tested range, with the hydrogen production FE approaching almost 100% after > -0.9 V. All HEA samples showed significantly lower selectivity to nitrite.

To investigate the origin of the current density and selectivity differences, the electronic structure of HEA samples was analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. S10-S12), which typically probes to a depth of about 10 nm for inorganic metallic materials [31]. In the Fe 2p spectrum, the peaks at 706.6, 710.0, 712.0, 714.8, and 718.8 eV are attributed to the metallic Fe, Fe²⁺, Fe³⁺, Fe²⁺ satellite, and Fe³⁺ satellite peaks, respectively (Fig. 3a) [32]. Subsequently, the surface etched with Ar plasma with an etching rate of 0.2 nm/s exhibited a notable increase in the intensity of the metallic Fe peaks with etching times up to 50 s and 100 s, while strong oxidation peaks remained present. A comparable phenomenon is observed in the Co 2p XPS spectrum, wherein the Co³⁺ peaks located at 778.2 and 782.7 eV and Co²⁺ peaks located at 780.2 and 786.2 eV. With prolonged etching time (Fig. 3b), the peak are Co³⁺/



Fig. 2. (a) LSV curves of Cu@C, HEA-0, HEA-10, and HEA-50. (b) FE of Cu@C, HEA-0, HEA-10, and HEA-50. (c) ammonia-producing sub-current of Cu@C, HEA-0, HEA-10, and HEA-50. (d) ammonia-producing yield rate of Cu@C, HEA-0, HEA-10 and HEA-50.



Fig. 3. (a-e) X-ray photoelectron spectroscopy (XPS) of HEA-0 samples etched for 0 min/1min/2min. (f, g) XPS-determined atomic percent XPS-determined atomic percentage-depth profile of HEA-0 and HEA-10 as a function of Ar^+ etching time.

 Co^{2+} nearly kept the same, , substantiating that the Co element was mainly present in its oxide form [33]. In the case of the Ni 2p XPS spectrum, the un-etched HEA-0 surface exhibits four distinct types of characteristic peaks, namely a metallic Ni (852.2 and 867.9 eV), Ni³⁺ (855.8 and 873.1 eV), Ni²⁺ (853.9 and 871.2 eV) and satellite peak (861.1 and 878.4 eV) (Fig. 3c) [34]. After Ar plasma etching, the peak pattern is consistent with that observed in Ni-based metal alloys, with the satellite and oxide peaks almost absent, suggesting that Ni exists in two forms: as an oxide phase on the surface and as a metal alloy phase within the interior [35,36]. The evolutionary trends observed in the Cu 2p and Pd 3d XPS spectra are consistent with those observed in the Ni 2p XPS spectra, which exist as an oxide on the surface of the HEA-0 and as an alloy in the interior (Fig. 3d and 3e) [37-41]. Obviously, under the presence of oxygen, the element across the electrocatalyst exhibits heterogeneous and gradient distribution. A comparable phenomenon is also observed in sample HEA-10, wherein the catalysts are observed to exist as ultrathin FeCoNiPdCu high-entropy oxides shell on the surface, FeCo-rich oxides@NiPdCu alloy within the middle layer, and FeCo-NiPdCu HEA in the innermost core (Supporting Information Fig. S13). It is noteworthy that no changes were observed in the C 1s spectrum, indicating that oxygen passivation did not alter the electronic structure of the carbon material (Supporting Information Fig. S14).

Then, the elemental atomic ratio analyses based on the XPS technique in Fig. 3f and 3g indicated a gradient distribution of Fe, Cu, and Pd elements in both the HEA-0 and HEA-10 samples. Ni and Co elements remained nearly the same. Specifically, for individual samples, the surfaces of both samples exhibit Cu and Pd enrichment; Fe is predominantly distributed in the bulk phase. The XPS full-spectrum analysis further confirms the surface enrichment of Cu and Pd (Fig. S10-12). Comparative analysis of samples passivated under different oxygen concentrations reveals that those exposed to higher external oxygen concentrations demonstrate increased Fe and reduced Pd surface content, as will be discussed in the subsequent analysis.

Based on the above experimental results, the prepared HEA-based catalysts were structurally characterized by the following main features: 1. gradient distribution of Fe, Cu, and Pd in HEA-0 and HEA-10, which is often observed in the FCC high entropy alloy [41,42]. As discussed above, the large differences in the atomic radius and electronegativity between the Pd and NiCoCuFe elements would decrease

homogeneity. 2. Both HEA-0 and HEA-10 exhibited FeCoNiCuPd highentropy oxide/FeCoOx@NiCuPd alloy/FeCoNiCuPd high-entropy alloy non-homogeneous multilaver structure, indicating in the strategy of preparing HEA using calcination-assisted reduction, a very thin oxide layer inevitably appeared on the surface of the catalysts, even if the catalysts were passivated with trace amount oxygen (Fig. 4a). Moreover, it should be noted that the surface oxidation passivation technique was strategically applied to establish an ultra-thin oxide layer through a precisely controlled oxidation process. This engineered passive film effectively inhibited the formation of a thick oxide scale that would otherwise develop during the material's natural cooling phase under ambient atmospheric conditions. Thus, HEA-0 exhibits a higher oxidation degree than other samples, which was also confirmed by the EIS characterization results (Supporting Information Fig. S15). In the EIS equivalent circuit, R1 and CPE1 are connected in parallel and then in series with R_s. Here, R_s represented the solution resistance, R₁ corresponded to the charge-transfer resistance, and CPE1 replaced the ideal capacitor [43]. The EIS data with a smaller semicircle radius indicated reduced charge-transfer resistance. The enhanced performance of HEA-10 could be attributed to its reduced surface oxide layer thickness since the metallic composites inherently exhibit higher electrical conductivity than their oxidized counterparts under identical conditions. 3. Fe tends to migrate toward the surface of HEA-0 compared to that of HEA-10 under the driving force of generating metal oxides. The binding ability between metal elements and oxygen during oxygen passivation could be measured by the formation of enthalpy. As shown in Fig. 4b, in the FeCoNiPdCu HEA system, the order of metal oxide formation enthalpy was Fe (Fe₃O₄, -1121 kJ/mol) < Co (Co₃O₄, -917 kJ/mol) < Ni (NiO, -239 kJ/mol) < Cu (CuO, -155 kJ/mol) < Pd (PdO, -58.99 kJ/mol), indicating a sequential decrease in the ability to form metal oxides, which could well explain the heterogeneous multilayer structure in the fabricated HEA-based catalyst.

After confirming the catalyst's composition and electronic structure, the electrochemical NO₃RR performance was well explained. For a single sample, the large differences in the atomic radius and electronegativity between the Pd and NiCoCuFe elements would decrease homogeneity. Specifically, the material's overall distribution of Ni and Co elements shows no significant changes. At the same time, Pd and Cu exhibited a gradient distribution with a noticeable decrease in atomic



Fig. 4. (a) Schematic illustration of the surface transformation process of high-entropy alloys in oxygen-containing environments (b) Enthalpy of formation of some metal oxides.

ratio from the surface to the bulk. In contrast, Fe was scarce on the surface but abundant in the bulk, forming a heterogeneous multilayer structure comprising FeCoNiPdCu high-entropy oxide/FeCo oxide@-NiPdCu alloy/FeCoNiPdCu high-entropy alloy. Importantly, previous research results suggested that Fe, Co, Ni, and Pd (four elements), have better hydrogen intermediate adsorption/desorption behavior (Pd $(\Delta G_{H} = -0.11 \text{ eV}) > \text{Co} (\Delta G_{H} = -0.20 \text{ eV}) > \text{Ni} > (\Delta G_{H} = -0.24 \text{ eV}) > \text{Fe}$ $(\Delta G_{\rm H} = -0.35 \text{ eV}))$ ($\Delta G_{\rm H}$: hydrogen adsorption free energy.). In contrast, Cu has a good affinity towards NO₃ adsorption/desorption ability [44,45]. Upon modulating the oxygen passivation process, it was found that increasing the oxygen partial pressure significantly raised the surface Fe content (attributed to differences in metal oxide formation enthalpies). In contrast, the thickened oxide layer reduced conductivity (as confirmed by EIS analysis). Consequently, the superior catalytic activity of HEA-10 was attributed to its thinner oxide layer, which ensured excellent conductivity, combined with surface enrichment of Cu and Pd elements.

3. Conclusion

In this study, three FeCoNiPdCu HEA-based samples were synthesized by modifying the post-treatment parameters. The resultant samples exhibit a heterogeneous multilayer structure comprising FeCoNiPdCu high-entropy oxide/FeCo oxide@NiPdCu alloy/FeCo-NiPdCu high-entropy alloy. Notable discrepancies in current density and selectivity were observed in the electrochemical nitrate reduction reaction, which could be attributed to variations in oxide layer thickness and the atomic ratio of Pd to Cu on the surface. Our work has deepened our understanding of the structure of HEA-based nanomaterials and advanced the analysis of the active sites and corresponding catalytic mechanisms.

CRediT authorship contribution statement

Hao Zhang: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Tianze Ren:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Xiuming Bu:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Chuqian** Xiao: Formal analysis, Data curation. Shaoyan Wang: Formal analysis, Data curation. Di Yin: Formal analysis, Data curation. Xiulan Hu: Writing – review & editing, Resources, Funding acquisition. Johnny C. Ho: Writing – review & editing, Writing – original draft, Supervision, Project administration. Xianying Wang: Writing – review & editing, Writing – original draft, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2025.163269.

Data availability

Data will be made available on request.

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