

Ordering-dependent hydrogen evolution and oxygen reduction electrocatalysis of high-entropy intermetallic Pt₄FeCoCuNi

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Disordered multi-component alloys with solid-solution structure (such as high-entropy alloys) have attracted wide research attention as robust electrocatalysts. In comparison, ordered multi-component intermetallic alloys have been hardly explored and the effects of the ordering degree of crystal structure on catalytic activity remain unknown. In this study, a series of multi-component intermetallic Pt₄FeCoCuNi nanoparticles with tunable ordering degrees were fabricated. Transformation mechanism of multi-component nanoparticles from disordered structure into ordered structure was revealed at the single-particle level using aberration-corrected STEM, which agrees with macroscopic analysis by SAED and XRD. The electrocatalytic performance of Pt₄FeCoCuNi nanoparticles correlates well with its crystal structure and electronic structure. It was found that increasing the degree of order promotes the electrocatalytic performance. The highly ordered Pt₄FeCoCuNi achieves the highest mass activities towards both acidic oxygen reduction reaction (ORR) and alkaline hydrogen evolution reaction (HER) which are 18.9-fold and 5.6-fold higher than those of commercial Pt/C, respectively. Experiment also shows that this catalyst demonstrates better long-term

stability than both partially ordered and disordered Pt₄FeCoCuNi as well as Pt/C when subject to both HER and ORR. This ordering-dependent structure-property relationship provides insight into the rational design of catalysts and stimulates the exploration of many other multi-component intermetallic alloys.

1. Introduction

The global need for decarbonization has accelerated the development of renewable energies.^[1] However, direct usage of renewable solar and wind energy on a large scale is limited by their intermittence.^[2-3] Water electrolysis has recently surfaced as an appealing green technology to convert and store intermittent electricity from renewable sources into chemical bonds by generating H₂ as a clean energy carrier^[1, 3-6] and O₂ as a by-product. The recombination of H₂ and O₂ producing water as the only product can generate electricity through hydrogen proton-exchange membrane fuel cells (PEMFCs), which are an attractive zero-emission power source for various applications such as vehicles.^[7-10] To achieve this hydrogen-based energy system at scale, rational design of Pt-based electrocatalysts is crucial to overcome the overpotential of the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), which are key half-reactions that determine the efficiency of water electrolyser and fuel cells.^[1, 11-14]

Alkaline water electrolysis (AWE) technology has dominated large-scale commercialization^[6, 11, 15-16] since acidic water electrolysis suffers from high equipment cost and sluggish kinetics of the anodic half reaction (i.e., oxygen evolution reaction). However, compared with acidic environments, the cathode made of Pt is typically less efficient by ~2 to 3 orders of magnitude in catalyzing HER in alkaline environments due to the lack of protons.^[3, 15, 17] This results from additional water dissociation where Pt has poor ability to supply protons in the first step of alkaline HER.^[3, 11, 18-20] Numerous efforts have been devoted to boosting alkaline hydrogen evolution via accelerating the kinetics of water dissociation.^[3, 11, 15-16, 18] For example, 3d-transition metal oxides are incorporated as the cathode since they have much stronger water dissociation ability than Pt.^[18] The composite of Ni(OH)₂ clusters on Pt (111) shows eight times higher alkaline HER activity than pure Pt (111) due to the collaborative effects between Ni(OH)₂ promoted water dissociation and Pt promoted proton recombination.^[18] On the other hand, the sluggish kinetics of cathodic oxygen reduction reaction (ORR) of PEMFCs technology also requires the Pt to overcome its high overpotential.^[1, 7, 18, 21-24] Deactivation of catalytic Pt nanoparticles due to sintering has also been a long-standing problem.^[25] Aggregation of Pt nanoparticles of commercial Pt/C under both HER, especially in

alkaline,^[13-14, 26] and ORR^[22, 27], results in decreased exposed surface area leading to poor atom utilization efficiency of Pt catalysts. Owing to the poor durability, high price and limited reserve of Pt, there is a pressing need to enhance the durability and activity while reducing the usage of Pt.^[9, 23-24, 28]

Alloying Pt with transition metals has been shown as an effective way to enhance the activity and durability of ORR^[17, 23] and HER^[29-30] while lowering the amount of Pt in electrocatalysts simultaneously. Compared with chemically disordered (random) solid-solution alloys in which all elemental atoms are randomly dispersed in the lattices (i.e., chemical/elemental disorder), intermetallic alloys feature elemental/chemical ordering between sublattices.^{[44][33]} Intermetallic alloys with defined surface composition and active sites with shortened bond length have shown enhanced durability and activity for both ORR and HER than their disordered alloy counterparts.^[31-32] The better electrocatalytic stability results from their shortened bond length and thus stronger heteroatomic bonding strength as well as higher thermodynamical stability than disordered alloys.^[33] However, most of these studies have so far focused only on binary intermetallics.

Recently, high entropy materials (HEMs) comprising multiple elements have attracted increased attention across various fields, such as electrocatalysis,^[34-35] batteries,^[36-38] thermoelectrics^[39-40], and structural materials.^[41-42] Besides large compositional space,^[43] HEMs offer the benefit of robust structural stability owing to the high configurational entropy caused by multi-elemental mixing and sluggish atomic diffusion.^[44] High-entropy stabilization strategies have successfully addressed the concern about stability of high-Ni cathodes for next-generation lithium-ion batteries.^[37] Besides robust structural stability and large compositional flexibility, HEMs have also attracted attention as electrocatalysts because each metallic atom in high entropy materials will cause a local *d*-band hybridization with possibly large number of combinations of neighboring elements.^[45] Consequently, this random *d*-band hybridization of multi-elemental mixing causes a near-continuous and broad binding energy distribution that enables HEMs to offer a wide range of adsorption sites, which is desirable for multistep reactions, like HER in alkaline and ORR.^[44] Inheriting the merits of both multi-component (i.e., high-entropy) solid-solution alloy and intermetallic alloys, multi-component intermetallics are potentially highly active and durable electrocatalysts. Despite the potential for multi-component intermetallics to be highly active and durable electrocatalysts, the mechanism of their crystal nucleation and growth, as well as

their electrocatalytic applications for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) have not been studied in detail due to the challenges in synthesis and characterization. Also, the effects of its varied crystal structures on electrocatalytic performance remain unexplored.

To address these issues, high-entropy intermetallic Pt₄FeCoCuNi alloy particles with tunable ordering degree are synthesized. Pt₄FeCoCuNi is chosen because all bimetallic PtFe,^[21] PtCo,^[31] PtNi,^[23] and PtCu,^[46] show enhanced ORR activity compared to Pt/C,^[47] and NiCu-,^[12, 48] NiCo-,^[49] and FeNi-based^[50] non-precious-metal based nanocatalysts also show excellent activity for alkaline HER. Ultrathin oxides and hydroxides were detected by surface-sensitive XPS on the surface of FeNi alloy exposed to air.^[51] Oxides and hydroxides are reported to be efficient in promoting water dissociation, although poor in recombining H_{ad} into H₂.^[17, 52-53] By contrast, Pt is efficient in hydrogen recombination but poor in water disassociation.^[11, 18-20] The synergistic effect that FeCoNiCu supply protons for nearby Pt to form H₂ is expected to enhance alkaline HER activity of Pt₄FeCoCuNi relative to Pt/C.^[18]

In this study, the ordering degree of multi-component intermetallic nanoparticles is precisely controlled through the tuning of annealing temperature and duration, and the ordering transformation is observed to take place from the edges of the nanoparticles. The relationship between crystal structure, electronic structure, and electrocatalytic performance is then analyzed. The results show that changes in crystal structure result in alterations in the electronic structures, including the position of the d-band center, which is widely recognized as a descriptor for both HER^[48] and ORR activity^[22, 54-56]. Specifically, the measured valence band spectrum shows that the highly ordered multi-component Pt₄FeCoCuNi experiences a downshift of d-band center relative to Pt, and therefore weakened adsorption of intermediates for HER and ORR. It is well-known that pure Pt surfaces show too strong adsorption of oxygen which makes oxygen desorption difficult.^[57] Besides the optimization of electronic structure, the improved water disassociation ability by the incorporation of FeCoCuNi is favorable for the alkaline HER. Electrochemical measurements show that the highly ordered high-entropy intermetallic alloy delivers high mass activity towards alkaline HER (71.9 A mg_{Pt}⁻¹ at -0.2 V vs reversible hydrogen electrode (RHE)), i.e., 2.1-fold, 3.0-fold and 5.6-fold higher than those of partially ordered, disordered Pt₄FeCoCuNi counterparts and Pt/C, respectively. Likewise, its acidic ORR mass activity (3.78 A mg_{Pt}⁻¹ at 0.9 V vs RHE) is enhanced by 2.1-fold, 4.4-fold and 18.9-fold as compared with those of partially ordered,

disordered Pt₄FeCoCuNi, and Pt/C, respectively. The ordered Pt₄FeCoCuNi demonstrates high structural stability and improved durability for both hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) due to the entropy increment resulting from multi-elemental mixing and the thermodynamically stable ordered intermetallic structure. The structure-performance relationship established in this work, which depends on the ordering degree, provides valuable guidelines for the design of highly durable and efficient electrocatalysts. Furthermore, the exceptional electrocatalytic performance of chemically ordered Pt₄FeCoCuNi serves as an incentive for the synthesis of additional multi-component intermetallic electrocatalysts.

2. Results and discussion

2.1. Synthesis

In this work, the sulfur-anchoring strategy^[33] is used to synthesize Pt-based intermetallics at nanoscale with an average particle size of around 5 nm (**Figure 1a**). The process starts with the synthesis of S-doped carbon (S-C) supports by carbonization of 2,2'-bithiophene with the addition of cobalt to increase the yield and silica nanoparticles to increase the surface area, respectively. Silica was then etched away by excessive 2.8 M NaOH for a duration of 6 days whilst cobalt species were removed by 3 M H₂SO₄ at 110 °C for 72h. The obtained S-C consists of C (83.4 wt%), S (10.8 wt%), O (4.9 wt%), Co (0.8 wt%) and Si (0.1 wt%) (Table S1, Supporting Information). Subsequently, a uniform mixed solution was produced by mixing of Pt-, Fe-, Co-, Cu-, Ni-precursor solutions with the assistance of sonication (Figure S1, Supporting Information). After that, the mixed metallic salts were loaded on the S-C support via a typical wet impregnation method followed by drying using a rotary evaporator. Finally, the dried black powder was annealed in Ar/H₂ with a flow rate of 115/15 sccm to form S-C supported Pt₄FeCoCuNi nanoparticles. Pt₄FeCoCuNi nanocrystals with different lattice structures were obtained upon the control of the heating temperature T and duration t .

2.2. Structural characterization

Field-emission scanning electron microscopy (FESEM) images show that S-C supports appear three-dimensional porous morphology (Figure S2, Supporting Information). The abundant pores endow S-C with a large surface to disperse metallic nanoparticles. SEM-EDS reveals that the weight percentage of S is 10.8 wt % in the S-C support with the S-to-C weight ratio of 12.9 % (Figure S3, Table S2, Supporting Information). XPS survey spectrum of the S-

C support (Figure S4a, Supporting Information) shows the characteristic core-level peaks of S and C. The composition is analysed using high-resolution S2p and C1s spectra (Figure S4b and S4c, Supporting Information). The weight ratio of S to C from the XPS analysis (around 12.1 %) is very close to the EDS results.

The crystal structures of the S-C supported Pt₄FeCoCuNi nanocrystals were investigated by powder X-ray diffraction (XRD) (Figure 1b). XRD patterns of the samples annealed at $T \geq 600^\circ\text{C}$ are well matched with the ordered *fcc* PtCo phases (PDF # 03-065-8969). The peaks including (001) at 24.0° and (110) at 32.8° are typical characteristics of ordered intermetallics, i.e., superlattice peaks. The change of the ordering degree was analyzed quantitatively by calculating the ratio of the peak areas (Figure 1c). The ratio of the (110) peak area to the sum area of the (111), (200) and (002) peaks, $S(110)/(S(111) + S(200) + S(002))$, is used to indicate the ordering degree.^[32] When T is reduced to 500°C , XRD patterns of samples in the absence of superlattice peaks agreed with disordered single-phase fcc PtCo phases (PDF #04-006-2778). The the broad hump at 23.5° originates from amorphous glass used as the support for XRD measurement (Figure S5a, Supporting Information). The XRD shows that both annealing temperature (T) and time duration (t) determine the crystal structure of the obtained nanocrystals. $T \geq 600^\circ\text{C}$ leads to an ordered structure, while $T = 500^\circ\text{C}$ leads to a disordered structure. Compared with solid-solution (i.e., disordered) alloys with featured chemical disorder, intermetallic alloys exhibit long-range chemical ordering. Transformation from disordered alloys to intermetallics needs to overcome thermodynamic barrier and slow kinetics.^[32] It is noted that at $T = 500^\circ\text{C}$, the XRD patterns show absence of characteristic superlattice peaks from intermetallic structure, but only those of ~~disordered~~ single-phase face-centered cubic (fcc) solid-solution alloy. Additionally, the single-phase fcc structure can even form at $T = 170^\circ\text{C}$ for $t = 5$ min, indicating a low energetic barrier for the formation of single-phase fcc solid-solution high-entropy alloy structure (Figure S5b, Supporting Information). In comparison, the ordered structure only forms when increasing T to 600°C . Therefore, we believe that $T \geq 600^\circ\text{C}$ is critical to ensure sufficient external energy to overcome the barrier for the chemical ordering transformation.

Increasing T from 600°C to 900°C for $t = 25$ min can further increase the ordering degree from 35% to 76%, indicating that higher temperature can accelerate the chemical ordering transformation by providing more energy to expedite the atomic diffusion required for the

crystal structure transformation. It is reasonable that annealing at a sufficiently high temperature for enough time can overcome energy barrier and accelerate the sluggish transformation kinetics. Meanwhile, when extending t from 25 to 120 min at $T = 700\text{ }^{\circ}\text{C}$, the degree of ordering increases from 52% to 65%, suggesting that extending t can also increase the degree of ordering. Transforming disordered alloys to ordered intermetallics is time-consuming due to the slow atomic diffusion. The results indicate that elevated temperatures and prolonged annealing times promote the ordering transformation. Elevated temperatures increase the atomic diffusion rate, while longer annealing times allow for a complete transformation. Hence, high temperatures and long annealing times are critical for the growth of highly ordered intermetallics. Notably, the ratio of Pt to the other four elements is essential in obtaining a single-phase intermetallic. Excessive Pt leads to mixed phases of fcc-Pt and intermetallic $\text{Pt}_4\text{FeCoCuNi}$ (Figure S6, Supporting Information). Compared with disordered $\text{Pt}_4\text{FeCoCuNi}$, the dominant (111) peak of highly ordered $\text{Pt}_4\text{FeCoCuNi}$ shifted to higher angles (Figure 1b), suggesting a shortened bond length and therefore stronger electronic interaction between neighbouring atoms.

The electrical conductivity of the S-C support of all samples can be gauged by looking at the characteristic peaks in Raman spectroscopy (Figure 1d). All the samples display two characteristic Raman features at around 1355 and 1598 cm^{-1} , which can be assigned to the D and G bands of the carbon matrix, respectively.^[58-59] The D and G bands correspond to the sp^3 disordered carbon and the ordered graphitic sp^2 carbon, respectively. The relatively high ratio of G band in all samples suggest that the obtained carbon supports is most likely graphitized and hence could have a higher electrical conductivity,^[60] which can facilitate electron transfer to realize an efficient electron transfer process in electrocatalytic reactions, including HER and ORR.^[61] In the following discussion, we denote the resultant nanocrystals annealed at $1000\text{ }^{\circ}\text{C}$ for 120 min, $700\text{ }^{\circ}\text{C}$ for 120 min, and $500\text{ }^{\circ}\text{C}$ for 25 min with the ordering degree of 0, 65% and 92% as the highly ordered, partially ordered, and disordered multi-elemental $\text{Pt}_4\text{FeCoCuNi}$ samples, respectively.

To investigate the microscopic crystal transformation mechanism, we characterize the atomic-scale ordering transformation pathway of single particles using aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 2a-e). HAADF-STEM images exhibit atomic number (Z) contrast where elements with higher atomic number contribute brighter contrast. For the highly ordered sample (Figure

2d and 2e), a periodic square array of dark Fe/Co/Ni/Cu columns surrounded by bright Pt columns along the [001] zone axis was observed. Also observed is a structure of alternating stacking of Pt columns (bright) and Fe/Co/Ni/Cu columns (dark) along the $[1\bar{1}0]$ zone axis as shown by the bright contrast, corresponding to the $L1_0$ ordered structure (Figure 2f and 2g). This alternating stacking of bright Pt columns and dark Fe/Co/Ni/Cu columns is further confirmed by the line profile alone (Figure 2h), which shows intensity contrast between the Pt columns and the Fe/Co/Ni/Cu columns. For partially ordered sample (Figure 2c), the top left shows a periodic square array structure, while the bottom right displays a chemical disordered structure. The STEM of the disordered sample displays chemical disordering, i.e., an disordered solid-solution structure. Fast Fourier transform (FFT) patterns further verify the corresponding disordered and ordered crystal structures, in good agreement with the corresponding XRD patterns. For the partially ordered sample, it is clear that its top left part has transformed into an intermetallic structure with chemical ordering, while its bottom right part still remains the chemically disordered structure. The STEM image of the partially ordered particle demonstrates that the ordering transformations nucleate at the surface and propagate deeper into the center. Otherwise, if the ordering transformation nucleates at the core and propagates out to the shell, an intermetallic-core/disordered-shell architecture would be observed, which contradicts with observed results. Therefore, nucleation should happen at the surface of nanoparticles where the surface energy is high. This is consistent with evidence that application of external energy, e.g., via Joule heating, can transfer a disordered alloy into a thermodynamically more stable ordered structure.^[62] Therefore, under reducing atmospheres at elevated temperatures, the metallic salts are first reduced and then crystallized to disordered solid-solution alloy. Afterwards, sustaining the high temperature for longer times promotes the gradual phase transition from disordered alloy to intermetallic. Because the atomic diffusion and lattice rearrangement take time to complete, incomplete ordering transformations lead to a partially ordered structure consisting of disorder and ordered structures. This has been demonstrated by both macroscopic XRD (Figure 1b) and localized STEM (Figure 2a, c and d). Therefore, the transition ordering is from disordered alloy to partially ordered structure and finally to fully ordered intermetallic structure. This is consistent with XRD results that both higher temperature and longer-duration heating enhance the degree of ordering. These crystal structural transitions are further verified by the selected-area electron diffraction (SAED) patterns (Figure 2i-k). The diffraction rings shown by the SAED patterns of disordered sample agree with facets of XRD results, confirming that the single-phase fcc solid-solution structure without superlattices. The SAED patterns of partially

ordered sample show the appearance of superlattice facets, corresponding to the appearance of ordering, which agrees well with XRD patterns. Compared with partially ordered sample, the diffraction rings corresponding to superlattice peaks in the SAED patterns of highly orderedly Pt₄FeCoCuNi such as (001) and (110) are much brighter, indicating increased percentage of ordered structure and thus an increased degree of ordering, further verifying the XRD results. To illustrate the chemically ordering transformation more clearly at atomic level, we built possible structural models of as-synthesized disordered, partially ordered, and fully ordered Pt₄FeCoCuNi nanoparticles (Figure 2l-n).

A series of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show that the S-C support contains both dense and uniform nanoparticles without aggregation (**Figure 3a-c**). Statistical analysis shows that the average particle sizes of disordered, partially ordered, and highly ordered samples are 5.1, 4.5, and 3.6 nm, respectively, with a narrow size distribution (Figure 3d-f). The obtained average size agrees with the previously reported size of bimetallic intermetallics synthesized by sulfur-anchor strategy.^[33] Owing to the high density and small size, the nanoparticles possess high specific surface area which enable abundant electrocatalytic active sites and high atom utilization. Statistical results of STEM show that commercial Pt/C has an average particle size of around 3.3 nm (Figure S7a-c, Supporting Information), which is consistent with that measured by the supplier, indicating that the statistical analysis of STEM images is reliable for estimating the average particle size of the studied samples.

STEM-EDS che mapping analysis shows uniform mixing of Pt, Fe, Co, Cu and Ni across the disordered Pt₄FeCoNiCu nanoparticles without any atomic segregation (Figure 3g), in good agreement with the single-phase fcc disordered alloy structure revealed by XRD. The successful synthesis of single-phase fcc Pt₄FeCoNiCu alloy is further validated by XRD analysis (Figure S8, Supporting Information). Because Pt has a larger atomic radius than Fe, Co Ni and Cu, the incorporation of Fe, Co Ni and Cu into Pt lattice causes lattice contractions. If Fe, Co, Ni and Cu are successfully alloyed with Pt without any phase separation, then Pt₄FeCoCuNi should experience a lattice contraction relative to pure Pt.^[25] This has been verified by the shifts of the XRD peaks to higher angles of the Pt₄FeCoCuNi samples compared with pure Pt, suggesting the successful alloying of Pt, Fe, Co Ni and Cu. Similarly, the homogenous dispersion of Pt, Fe, Co Ni and Cu elements across the highly ordered nanoparticles (Figure 3i) is consistent with the intermetallic alloy structure shown by XRD.

As a mixture of disordered and ordered alloy, partially ordered samples also show uniform mixing of the five elements in individual nanoparticles. The EDS-line scanning of a single particle further confirms that all the five elements are distributed uniformly in the studied samples (Figure 3j-l). This confirms the successful alloying of the five elements and such multi-elemental mixing leads to the entropy increment. The SEM-EDS spectra (**Figure 4a**) confirm the existence of Pt, Fe, Co, Cu, Ni, and show that the metallic compositions are comparable, while the higher ordered sample contains reduced S content. The decreased S content is due to heating at higher temperature and longer time.^[33] Both macroscopic SEM-EDS and localized STEM-EDS show consistent results about the ratio of Pt/Fe/Co/Cu/Ni (Figure S9, Table S2 and S3, Supporting Information).

The effects of crystal structure on electronic structure are investigated by measuring the valence band spectra (VBS) that determines the *d*-band center of Pt₄FeCoCuNi using X-ray photoelectron spectroscopy (XPS) (Figure 4b). After background subtraction using Shirley algorithm, the calculated centroid, marked by the short horizontal line, is taken as the corresponding *d*-band center position. According to *d*-band theory^[63-66], the *d*-band center plays a critical role in determining the adsorption strength of electrocatalytic intermediates.^[63-66] Specifically, a downward shift of the *d*-band center will lead to increased filling of adsorbate-metal antibonding states and therefore a weaker adsorption, and vice versa. Based on ORR volcano curve,^[57] Pt has too strong adsorption for oxygen on the surface and a slightly weakened adsorption will enhance its ORR performance. Compared with Pt₄FeCoCuNi, the support material (bare S-C) measured as a control has negligible contributions to the VBS, suggesting that the VBS differences of Pt₄FeCoCuNi with different ordering degrees result from the Pt₄FeCoCuNi particles themselves rather than the S-C support (Figure S10, Supporting Information). The VBS results exhibit that all the Pt₄FeCoCuNi samples show a downshift relative to pure Pt and thus possess relieved adsorption energy of oxygen on their surface. The *d*-band center of Pt₄FeCoCuNi is crystal-structure dependent since the samples with different ordering degrees have different *d*-band center positions. The *d*-band center position of the highly ordered sample is closest to the Fermi level, and there is a downshift trend in the *d*-band center from highly ordered, partially ordered to disordered samples. Therefore, increasing the ordering degree results in an upward shift of the *d*-band center.

XPS was further conducted to determine the bonding states of metallic elements. All the characteristic core-level peaks of Pt, Fe, Co, Ni, Cu and C corresponding to their compositions can be observed from the XPS survey spectrum (Figure S11, Supporting Information). As shown in Figure 4c-e, both metallic Pt peak and Pt-S peak can be observed in the disordered, partially ordered, and fully ordered Pt₄FeCoCuNi samples, among which disordered sample has the highest portion of Pt-S bonding due to the highest S content (Figure S12, Supporting Information). Compared with bare S-C support, the S2p peak shifts to higher binding energy by 0.12 eV after loading the Pt₄FeCoCuNi nanoparticles, suggesting a transfer of electrons from S to metals (Figure S13, Supporting Information). A new peak is observed at around 162 eV that can be assigned to S-metals bonding. To identify the metal that has been bonded to S, serious sintering is observed for S-C supported Pt-absent FeCoCuNi samples (Figure S14, Supporting Information) by removing the Pt precursor. This observation suggests that the S-metal bonding is, in fact, bonded between S and Pt. Such a Pt-S bonding is reported to play a key role in suppressing the sintering of Pt-based nanoparticles up to 1000 °C.^[33] XPS results show that both Ni and Co are mainly in their metallic states with small proportions in hydroxides (Figure S15 and S16, Supporting Information). The small peaks of hydroxides might be formed after exposure to air in high ambient humidity (RH > 80%) due to the high reactivity of these elements. By contrast, Cu2p peak can be fitted by only one metallic component, suggesting that Cu is less reactive than Co and Ni in the synthesized nanoparticles (Figure S17, Supporting Information). However, the Fe2p peaks were not assignable because of their overlap with both Co LMM Auger peak (713 eV) and Ni LMM Auger peak (713.7 eV) (Figure S18, Supporting Information).

The surface area and pore distribution of carbon matrix encapsulating nanoparticles were investigated using Brunauer-Emmett-Teller (BET) analysis (Figure S19 and Table S4, Supporting Information). The sulfur-carbon matrix has a large surface of 690.8 m² g⁻¹ and abundance mesopores (pore volume: 0.85 cm³ g⁻¹) with an average pore size of 58.2 Å. The highly ordered, partially ordered and disordered Pt₄FeCoCuNi samples inherit the porous structure of the bare S-C and show comparable surface pore sizes, which are 63.1, 63.5, and 63.8 Å, respectively (Figure 4f-k). These mesopores facilitate mass transfers, such as the deep penetration of electrolyte and rapid release of H₂ bubbles. For ORR, such mesopores are large enough for oxygen molecule to approach the catalysts surface and therefore can promote mass transfer. In comparison, small micropores (i.e., < 2 nm) cause a large gas diffusion resistance.^[67-68] -SO₃H in Nafion added as a binder that has too strong adsorption on Pt can

block the active sites, resulting in poor utilization of Pt.^[67-68] Encapsulating nanocatalysts into mesoporous carbon can avoid this negative effect by $-\text{SO}_3\text{H}$ inhibitions by separating nanocatalysts and Nafion while enabling efficient gas/mass diffusions. As a result, around 6.3 nm mesopores of the three catalysts have been shown to be desirable for ORR.^[69] For HER, the large surface area and abundant mesopores can separate the formed H_2 bubbles efficiently to keep the catalysts exposed to reactants, so as to maintain the high catalytic activity.

2.3. HER electrochemical performance

To correlate the crystal structure with electrocatalytic activity, we first tested HER performance of the disordered, partially ordered, and highly ordered samples as well as control samples in a standard three-electrode system in 1 M KOH aqueous solution. As shown by linear sweep voltammetry (LSV) (**Figure 5a**), the bare S-C shows negligible HER activity compared with other catalysts. The highly ordered $\text{Pt}_4\text{FeCoCuNi}$ needs an overpotential of only 20 mV vs RHE to deliver 10 mA cm^{-2} (η_{10} , commonly used performance metric for HER), which are much lower than the partially ordered and disordered $\text{Pt}_4\text{FeCoCuNi}$ counterparts (32 and 47 mV respectively) as well as commercial Pt/C (38mV) reference. Lower overpotential means less energy waste, which is therefore desired for catalytic applications. The measured η_{10} of Pt/C (38 mV) is consistent with previous reports (Table S5, Supporting Information), demonstrating the reliable HER measurement in this work. Tafel plots derived from LSV curves show that the highly ordered $\text{Pt}_4\text{FeCoCuNi}$ possesses the smallest Tafel slopes (31 mV dec^{-1}), suggesting its considerably enhanced alkaline HER kinetics (Figure 5b and 5e). The comparison of LSV curves normalized by mass loading of Pt also show that the highly ordered $\text{Pt}_4\text{FeCoCuNi}$ exhibits much better alkaline HER activity than both the partially ordered and disordered $\text{Pt}_4\text{FeCoCuNi}$ as well as the commercial Pt/C (Figure 5c). For practical industrial application of large-scale H_2 production, electrocatalysts have to operate under large overpotential to deliver large current density. Therefore, we compare the mass activity at the potential of -0.2 V vs RHE, it is $71.9 \text{ A mg}_{\text{Pt}}^{-1}$ for the highly ordered $\text{Pt}_4\text{FeCoCuNi}$, 2.1, 3.0, and 5.6 times higher than those of the partially ordered and disordered $\text{Pt}_4\text{FeCoCuNi}$ counterparts (34.8 and $23.8 \text{ A mg}_{\text{Pt}}^{-1}$ respectively) and commercial Pt/C ($12.9 \text{ A mg}_{\text{Pt}}^{-1}$), respectively (Figure 5d). These comparisons demonstrate that crystal structure plays a vital role in governing the alkaline HER activity and increased ordering degree can enhance the alkaline HER activity. All the synthesized $\text{Pt}_4\text{FeCoCuNi}$ catalysts exhibit much higher HER activity than commercial Pt/C at the large overpotential of -0.2 V. The activity enhancement relative to Pt/C could be attributed to the improved water

dissociation after introducing FeCoCuNi into the lattice of Pt.^[18] The highest alkaline HER activity of the highly ordered Pt₄FeCoCuNi is likely due to synergistic effects between the alternating stacking of Pt columns that promote proton recombinations and the Fe/Co/Ni/Cu columns that promote water dissociations. Besides, its optimized adsorption energy, as manifested by the moderate d-band center position, also contributes to enhanced HER activity. The alkaline HER performance metric, including η_{10} and Tafel slope, of Pt-based electrocatalysts reported in recent years have been summarized and compared with the synthesized nanocrystals in Figure 5f and Supporting Information (Table S6), which well position the highly ordered Pt₄FeCoCuNi among the best Pt-based electrocatalysts for catalyzing alkaline HER.

The durability of as-synthesized electrocatalysts was assessed by more than 50 h of chronopotentiometry (CP) at a current density of 10 mA·cm⁻² (Figure 5g) in 1M KOH electrolyte. The stability improves in the order of commercial Pt/C << disordered sample < partially ordered sample < highly ordered sample. Among these electrocatalysts, the highly ordered Pt₄FeCoCuNi shows the minimum potential increase of η_{10} and thus a negligible degradation. This indicates that the higher ordered Pt₄FeCoCuNi is the most durable alkaline HER catalyst, and the Pt₄FeCoCuNi catalyst deactivates fast as the ordering degree decreases. The excellent durability of the highly ordered Pt₄FeCoCuNi is further verified by the nearly overlapped LSV curves before and after the long-term HER stability test (Figure 5h). The improved durability of higher ordered Pt₄FeCoCuNi compared with disordered and partially ordered counterparts clearly demonstrates the critical role of ordered structure in the enhancement of alkaline HER durability. The ordered structure with increased bonding energy has been reported to boost electrocatalytic activity and durability compared with disordered structure.^[70-71] Compared with the Pt₄FeCoCuNi catalysts, commercial Pt/C deactivates much faster, suggesting that the key role of high entropy due to multi-elemental mixing in the enhanced durability of Pt₄FeCoCuNi catalysts. The alkaline HER durability of Pt/C were consistent with previous report.^[13-14, 26] The STEM image and mappings of Pt/C after 50 h alkaline HER stability test show the disappearance of the initial well-dispersed Pt nanoparticles, instead, long Pt rods and large Pt aggregates can be observed (Figure S20, Supporting Information). This remarkable morphology variation reveals that Pt nanoparticles of Pt/C suffer from severe aggregation during alkaline HER, which reduced exposed surface area and thus the reduced number of active sites for catalyzing HER. The severe aggregation of Pt/C explains the rapidly deteriorated HER activity. By contrast, STEM-EDS mapping and

line scan show absence of obvious elemental leaching for highly ordered Pt₄FeCoCuNi after durability test (Figure 5i and 5j). A series of characterizations show both the morphology and crystal structure of highly ordered Pt₄FeCoCuNi are maintained well after the durability test (Figure 5k-m, Figure S21-23, Supporting Information). The combination of the intermetallic structure and high entropy mixing of multiple elements endows highly ordered Pt₄FeCoCuNi with excellent structural stability and therefore exceptional catalytic durability. To sum up, both the activity and durability highly depend on the crystal structure (the degree of ordering) and exhibit the same trend in the order of commercial Pt/C < disordered sample < partially ordered sample < highly ordered sample. The high-entropy and intermetallic mechanism in boosting the durability may provide insights for designing more durable electrocatalysts across similar vast compositional spaces.

2.4. ORR electrochemical performance

The electrocatalytic ORR performance of the as-synthesized electrocatalysts was evaluated and benchmarked with commercial Pt/C using a rotating disc electrode (RDE) in 0.1 M HClO₄. The bare S-C as a control exhibits negligible ORR activity (Figure S24, Supporting Information). ORR polarization curves of different catalyst samples (**Figure 6a**) show that the half-wave potential ($E_{1/2}$) for the highly ordered Pt₄FeCoCuNi was 0.943 V, which is higher than those of the partially ordered and disordered counterparts (0.927 and 0.910 V, respectively). To further compare the intrinsic ORR activity, kinetic current is calculated using Koutecky-Levich equation^[22] and the mass activity is obtained by normalizing the kinetic current to the mass loading of Pt. The highly ordered Pt₄FeCoCuNi delivers a mass activity of 3.78 A mg_{Pt}⁻¹ at the generally chosen potential 0.9 V vs RHE, outperforming those of the partially ordered and disordered samples (1.84 and 0.86 A mg_{Pt}⁻¹, respectively) (Figure 6b). On the basis of the observed catalytic activity comparisons of the samples, it is clear that the distinct ORR activity can be correlated to the degree of ordering, i.e., higher ordering samples exhibit higher ORR activity. Notably, all the Pt₄FeCoCuNi catalysts exhibit significant higher $E_{1/2}$ than commercial Pt/C (0.861 V), suggesting enhanced ORR activity after mixing with FeCoNiCu. This is further confirmed by the comparison that the mass activities of the highly ordered, partially ordered and disordered Pt₄FeCoCuNi are 18.9-fold, 9.2-fold, and 4.3-fold higher than Pt/C (0.20 A mg_{Pt}⁻¹), respectively. The measured mass activity of Pt/C agrees well with previous reports.^[22-23, 28] The enhanced ORR activity can be attributed to optimized electronic structure (i.e., d-band center) after mixing with FeCoNiCu. This is because the strong oxygen adsorption energy of Pt tends to be weakened in the

Pt₄FeCoCuNi, which is manifested by the downshifted *d*-band center. The comparison of Tafel slopes using mass activities of the highly ordered, partially ordered and disordered Pt₄FeCoCuNi (51.5, 57.3, 64.1 mV decade⁻¹, respectively) as well as Pt/C (77.9 mV decade⁻¹) shows that the highly ordered sample has the smallest Tafel slope, indicating its faster kinetics for ORR of the studied catalysts (Figure 6c). LSV curves at different rotation speeds were further recorded (Figure S25, Supporting Information). Using the Koutecky-Levich plot (Figure 6d) obtained from polarization curves at different rotation speeds, the number of transferred electrons for ORR of the highly ordered Pt₄FeCoCuNi can be obtained, which is 3.98, suggesting that the catalyst favors the most efficient four-electron pathway from O₂ to H₂O. The ORR activity of the highly ordered Pt₄FeCoCuNi is further compared with those of earlier reported Pt-based ORR nanocatalysts (Table S7, Supporting Information), which positions the highly ordered Pt₄FeCoCuNi in this work among the best Pt-based nanocatalysts for catalyzing ORR in acid electrolytes.

To assess the ORR durability in acid, the ORR polarization curves before and after 30,000 cycles were compared via accelerated durability testing (ADT) between 0.5 and 1.1 V (Figure 6e-h). The $E_{1/2}$ of the highly ordered Pt₄FeCoCuNi is negatively shifted by 7 mV, much smaller than the 13 mV and 28 mV of the partially ordered and disordered counterparts, respectively. This result that the ordered multi-elemental sample shows more robust ORR durability than the disordered counterpart is consistent with that previously reported on bimetallic systems.^[31] The commercial Pt/C exhibits a notable activity drop, i.e., with the largest negative shift of $E_{1/2}$ after cyclings, in agreement with previous reports,^[23] suggesting that high entropy of the Pt₄FeCoCuNi samples can promote the ORR durability. After 30k cycles, the mass activity of the highly ordered Pt₄FeCoCuNi remains a very high value, i.e., 2.77 A mg_{Pt}⁻¹, with a small drop of 26 %, indicating its excellent durability (Figure S26, Supporting Information). By contrast, the mass activities of the partially ordered and disordered counterparts drop by 44 % and 62%, respectively, indicating that ordered structure can promote ORR durability owing to shortened bond length **from a stronger bonding**. After durability test, all the multi-component catalysts still have considerably higher mass activity than commercial Pt/C reference, demonstrating the enhanced ORR durability due to entropy increment after mixing with FeCoCuNi. Furthermore, both SAED and XRD analysis show that the highly ordered Pt₄FeCoCuNi still maintains the intermetallic crystal structure after the ORR durability test (Figure 6i, Figure S23, Supporting Information). A negative shift of the dominant (111) peak observed after the durability test suggests a lattice expansion caused by

leaching of non-noble metals which have small atomic radius. Both the STEM-EDS mapping and the line scan analysis show that the highly ordered Pt₄FeCoCuNi evolved into a core/shell architecture with a Pt-rich shell, which confirms the leaching and dissolution of non-noble metals under acidic ORR conditions (Figure 6j and 6k). The STEM image that shows a core with the alternating bright and dim contrasts and a shell with only bright atomic column verifies that it is an intermetallic-core/Pt-shell structure and the shell consists of three to four Pt atomic layers (Figure 6l, Figure S27a-d, Supporting Information). Structural model of such Pt₄FeCoCuNi intermetallic-core/Pt-shell nanoparticles was built to illustrate the atomic arrangements (Figure 6m). Interestingly, the STEM image shows that the disordered Pt₄FeCoCuNi also evolved into an alloy-core/Pt-shell structure (Figure 27c and 27d, Supporting Information). Finally, the STEM image shows an absence of significant agglomerations under ORR and the initial nanoparticle morphology were well maintained (Figure S28, Supporting Information). In contrast, apparent particle aggregations are observed for Pt/C after the durability test (Figure S29, Supporting Information). Interestingly, separated Pt nanoparticles can still be observed after ORR, which means that the Pt/C is less stable under alkaline HER than under acidic ORR.

3. Conclusion

A series of Pt₄FeCoCuNi nanocrystals with controllable ordering degree are fabricated. The crystal structural transformation is investigated using ex-situ techniques at multilength scales. It is found that the chemical ordering processes typically start from the the edge of nanoparticles. The controllable ordering degree endow Pt₄FeCoCuNi nanocrystals with tunable electronic structures, such as the *d*-band center position. The highly ordered quinary intermetallics possess the most optimized electronic structure and exhibit superior electrocatalytic activities for both HER and ORR than less-ordered counterparts and the commercial Pt/C. Such an enhanced performance is mainly attributed to the highly ordered crystal structure introduced electronic structure and surface structure. While Pt/C showed poor alkaline HER stability and also acidic ORR stability, bifunctional highly ordered Pt₄FeCoCuNi shows little activity decay after 50 h HER stability test and 30,000 potential ORR cycles. The excellent catalytic stability for HER and ORR can be attributed to combined effects of highly ordering crystal structure and high entropy. Besides offering a novel, efficient and robust HER and ORR nanocatalyst, the ordering-dependent structure-performance relation established from our work will provide guidance for rational design of

catalysts and call for further study of multi-component intermetallic materials for electrocatalysis.

4. Experimental Section

Materials: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AgNO_3 , $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, PdCl_2 , HAuCl_4 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, IrCl_3 , Nafion solution, Potassium hydroxide (99.99% trace metals basis, KOH), perchloric acid (HClO_4 , 70%, 99.999% trace metals basis) were purchased from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt% loading, Pt nanoparticles with diameter of ~ 3 nm supported on carbon) was purchased from Johnson-Matthey. Deionized (DI) water with a sensitivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ from the ELGA CHORUS 1 (Chemoscience Pte Ltd) was used all the time in this work.

Synthesis of S-C support: First, 1.0 g 2,2'-bithiophene and 0.5 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed in 60 ml Tetrahydrofuran (THF) and sonicated for 10 min. 1.0 g SiO_2 (5-15 nm particle size) was then added into the solution and dispersed by stirring for 4 h to yield a homogeneous mixture. Next, the mixture was dried in a rotary evaporator at 40°C . The dried powder was collected and annealed in an inert atmosphere achieved by a flux gas of Ar at a flow rate of 200 sccm (standard cubic centimetres per minute) at 750°C for 2 hours. After reaction, the furnace was cooled down to room temperature naturally. After annealing, the powder was added to 500 ml of 2.8 M NaOH and stirred for 6 days to perform alkaline leaching to remove SiO_2 templates. Afterwards, the product was added to 500 ml 3M H_2SO_4 and stirred at 110°C for four days to etch away Co species. Finally, the sample was washed by deionized water for six times and dried at 60°C in a vacuum oven overnight to obtain the S-C supports.

Synthesis of $\text{Pt}_4\text{FeCoCuNi}$ with different degree of ordering: The S-C supported catalysts are synthesized using an impregnation method. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were separately dissolved in deionized water to get 0.1 M solution, respectively. Then H_2PtCl_6 , FeCl_2 , NiCl_2 , and CoCl_2 precursor solutions with atomic ratio of 4:1:1:1 for Pt:Fe:Ni:Co were mixed and sonicated to form a uniform solution. Then a certain amount of S-C support was added into the solution and the weight ratio of the S-C to total metal content in precursors was fixed at 3:1 in all electrocatalysts synthesis. The mixture was stirred overnight and sonicated for two hours and then dried using rotary evaporator. The dried sample was ready for annealing at different temperatures for different durations to obtain different crystal structures (different degree of ordering). In a typical synthesis of carbon-encapsulated highly ordered sample, the product was annealed in a flowing Ar/ H_2 with a flow rate of 115/15 sccm at 1000°C for two hours. For the preparation of the partially

ordered sample and disordered sample, the annealing condition were changed to 700 °C for 120 min and 500 °C for 25 min, respectively. The annealing conditions, i.e., the annealing temperature and time durations, were changed to obtain the samples with varied ordering degrees.

Structural characterization: The SEM imaging was performed in a FESEM JEOL JSM-7600F with an accelerating voltage of 15 kV. The SEM EDS was performed in a FESEM JEOL JSM-7800F PRIME equipped an Oxford EDS detector with the capable of very fast EDS data collection and analysis. The sample for SEM-EDS was prepared by directly drop-casting onto an Al stub without introducing additional carbon. The TEM, STEM images, and the STEM-EDS mapping and line scan were acquired in a JEOL ARM-200F microscope equipped with JEOL delta aberration corrector and a cold field emission gun operating at 200 kV. The XRD data were acquired using a Bruker D8 Advance machine using Cu K α as the X-ray source. The XPS data were collected by a XPS Kratos AXIS Supra spectrometer using a monochromatic Al K α source. The XPS machine was operated at 15 mA and 15 kV and the Au 4f $_{7/2}$ peak at 84.0 eV was used as the reference (Figure S30, Supporting Information). Raman spectra were collected using a WITec Alpha confocal Raman instrument with the excitation laser wavelength of 532 nm. Calibration with the Si peak at 520 cm $^{-1}$ was conducted before each Raman spectrum measurements. BET data were collected on a highly automated TriStar II setup.

Electrochemical measurement: Electrochemical tests were performed on Metrohm Autolab (PGSTAT302N) electrochemical workstation using a standard three-electrode setup. For all performance tests, a graphite rod was used as the counter electrode, while a glassy carbon electrode (5 mm inner diameter) was used as the working electrode. Mercury-mercury oxide (Hg/HgO, filled with 1M KOH solution) was used as the reference electrode in alkaline environments while a silver chloride reference electrode (Ag/AgCl, filled with saturated KCl solution) was used in acidic environments. 1M KOH was used as electrolyte for alkaline HER performance tests while 0.1M HClO $_4$ was used as electrolyte for acidic ORR performance tests, respectively. Before each electrochemical measurements, calibration of reference electrodes was performed by scanning hydrogen evolution reaction/hydrogen oxidation reaction cyclic voltammetry (CV) (scan rate: 2 mV s $^{-1}$) using Pt foils as both the working electrode and the counter electrode in H $_2$ -saturated 1M KOH for the Hg/HgO electrode or 0.1M HClO $_4$ for the Ag/AgCl electrode (Figure S31 and S32, Supporting Information). The average values of the two potential intercepts at the zero current point were calculated to be -0.266 V for the Ag/AgCl reference electrode and -0.9265 V for the Hg/HgO reference

electrode, respectively. All potentials measured against the Hg/HgO or Ag/AgCl were converted to be vs. reversible hydrogen electrode (RHE) reference scale based on calibrated values by using equations of $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.266 \text{ V}$ or by $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.9265 \text{ V}$. All potentials were iR-corrected. Working electrodes were prepared by depositing catalyst ink onto the glassy carbon electrode. To prepare catalyst ink, 1.0 mg catalysts were dispersed into 1.0 ml mixed solution containing 750 μL deionized water, 230 μL ethanol, and 20 μL Nafion, followed by sonication for 5 h. Before dropping catalyst ink, the glassy carbon working electrode was polished by 0.05 μm diameter alumina slurry to a near-mirror finish, which was followed by repeated sonication in deionized water. After drying the well cleaned glassy carbon disk in ambient condition, a total of 10 μl of the as-prepared catalyst ink was deposited on the glassy carbon disk of the RDE, followed by drying in ambient condition. The Pt loadings for the highly ordered, partially ordered, disordered and Pt/C catalysts are controlled at 8.57, 8.47, 7.09, and 10.2 $\mu\text{g per cm}^2$ (normalized over the geometric area of 0.196 cm^2), respectively. The Pt loading of Pt/C is close with previous report.^[22-24]

HER linear sweep voltammetry (LSV) was recorded with a potential scanning rate of $5 \text{ mV} \cdot \text{s}^{-1}$ with a step size of 2.44 mV in 1M KOH while HER CVs were recorded with a potential scanning rate of $10 \text{ mV} \cdot \text{s}^{-1}$ in 1M KOH. The HER durability test was carried out via Chronopotentiometry at a current of $10 \text{ mA} \cdot \text{cm}^{-2}$ for 50 h. ORR polarization curves were recorded with a scanning rate of $10 \text{ mV} \cdot \text{s}^{-1}$ in O_2 -saturated 0.1M HClO_4 . ORR accelerated durability testing (ADT) was conducted within the voltage window of 0.5~1.15 V vs RHE with a scanning rate of $10 \text{ mV} \cdot \text{s}^{-1}$ in O_2 -saturated 0.1M HClO_4 . Using iR-corrected ORR polarization curves, the kinetic current (j_k) is obtained via the Koutecký–Levich equation:

$$j_k = (j_D \times j) / (j_D - j) \quad \text{Equation (1)}$$

where j_D and j are diffusion-limiting current and the measured current at a given potential, respectively. The ORR mass activity is obtained by normalizing the kinetic activity to the loading mass of Pt.

The number of transferred electrons at diffusion-limiting current region ($0.2 < E < 0.8 \text{ V}$) can be calculated using the

$$j_D = xnFD^{2/3} v^{-1/6} C\omega^{1/2} \quad \text{Equation (2)}$$

where x is 0.201 for ω in units of rpm, n is the number of electrons transferred for oxygen reduction, F is the Faraday constant, D is the diffusion coefficient of O_2 ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v is kinematic viscosity of the electrolyte ($1.009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), and C is the concentration of

dissolved oxygen ($1.26 \times 10^{-3} \text{ mol L}^{-1}$).^[72] The number of transferred electrons in a mixed kinetic-diffusion control region ($0.8 < E < 1.0 \text{ V}$) can be determined from the Levich plot.

Statistical Analysis: Each histogram in Figure 3d-f includes the statistic analysis of the size distribution for about 200 nanoparticles in each sample. The ‘Distribution Fit’ function under “Statistics“ of OriginPro 2019b was used in the statistical analysis to obtain the standard deviation (SD) values.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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The table of contents

Ordering transformation mechanism of high-entropy alloy Pt₄FeCoNiCu nanoparticles from disordered fcc to ordered fct intermetallic structure has been demonstrated by atomic-resolution AC-STEM and macroscopic SAED and XRD. Their electrocatalytic HER and ORR activities are revealed to be ordering-dependent and ordered Pt₄FeCoNiCu outperforms most Pt-based catalysts for catalyzing HER and ORR with robust durability.

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Ordering-dependent hydrogen evolution and oxygen reduction electrocatalysis of high-entropy intermetallic Pt₄FeCoCuNi