Fast site-to-site electron transfer of high-entropy alloy nanocatalyst driving redox electrocatalysis

Hongdong Li¹, Yi Han¹, Huan Zhao¹, Wenjing Qi², Dan Zhang¹,³, Yaodong Yu¹, Wenwen Cai¹, Shaoxiang Li³, Jianping Lai¹✉, Bolong Huang⁴✉ & Lei Wang¹,³✉

Designing electrocatalysts with high-performance for both reduction and oxidation reactions faces severe challenges. Here, the uniform and ultrasmall (~3.4 nm) high-entropy alloys (HEAs) Pt₁₈Ni₂₆Fe₁₅Co₁₄Cu₂₇ nanoparticles are synthesized by a simple low-temperature oil phase strategy at atmospheric pressure. The Pt₁₈Ni₂₆Fe₁₅Co₁₄Cu₂₇/C catalyst exhibits excellent electrocatalytic performance for hydrogen evolution reaction (HER) and methanol oxidation reaction (MOR). The catalyst shows ultrasmall overpotential of 11 mV at the current density of 10 mA cm⁻², excellent activity (10.96 A mg⁻¹Pt at −0.07 V vs. reversible hydrogen electrode) and stability in the alkaline medium. Furthermore, it is also the efficient catalyst (15.04 A mg⁻¹Pt) ever reported for MOR in alkaline solution. Periodic DFT calculations confirm the multi-active sites for both HER and MOR on the HEA surface as the key factor for both proton and intermediate transformation. Meanwhile, the construction of HEA surfaces supplies the fast site-to-site electron transfer for both reduction and oxidation processes.

https://doi.org/10.1038/s41467-020-19277-9

¹Key Laboratory of Eco-chemical Engineering, Key Laboratory of Optic-electric Sensing and Analytical Chemistry of Life Science, Taishan Scholar Advantage and Characteristic Discipline Team of Eco Chemical Process and Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 266042 Qingdao, P. R. China. ²College of Chemistry, Chongqing Normal University, 401331 Chongqing, P. R. China. ³Shandong Engineering Research Center for Marine Environment Corrosion and Safety Protection, College of Environment and Safety Engineering, Qingdao University of Science and Technology, 266042 Qingdao, P. R. China. ⁴Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Horn, Kowloon, Hong Kong SAR, China. ✉email: jplai@qust.edu.cn; bhuang@polyu.edu.hk; inorchemwl@126.com
Electrocatalytic processes play a vital role in energy conversion and reducing the environmental pollution\textsuperscript{2-5}. To improve the activity, selectivity, and stability of the catalytic reaction, it is necessary to develop high-performance advanced catalysts that can meet the needs of rapid development\textsuperscript{6-12}. High-entropy alloys (HEAs) have attracted wide interest as catalytic materials in the past few years\textsuperscript{13-16}. The alloy contains five or more elements which have similar atomic ratios\textsuperscript{16,17}. The atomic size of each component is different, which can cause lattice distortion\textsuperscript{18}. Besides, the presence of multiple components is conducive to promoting the formation of the solid solution phase and inhibiting the movement of dislocations. These characteristics of HEA lead to some unique characteristics, such as strong fracture toughness, corrosion resistance, and high mechanical strength\textsuperscript{19-21}. The ultimate goal of HEA is to adapt these characteristics to any desired response by using almost infinite possible combinations of elements and modifying their composition. In catalysis field, the adsorption of molecules and intermediates species on the surface of the catalyst affects the catalytic activity\textsuperscript{22}. These adsorption energies can be adjusted by allowing as compared to pure elements to increase catalytic activity\textsuperscript{23-25}. Recently, some HEAs had used as catalysts for electrocatalytic reactions, which display superior stability and catalytic selectivity and activity compared with traditional alloys\textsuperscript{13,26-30}. However, the traditional method mainly produce bulk HEAs rather than nanostructures\textsuperscript{26,31-34}. Moreover, the preparation of uniform nanostructured HEAs with small size (<10 nm) currently requires specific equipment (fast heating/cooling rate, ~10\textsuperscript{5} K per second), high temperature (~2000 kelvin), and high temperature resistant and conductive substrate (carbon nanofiber), such as carbon-thermal shock method\textsuperscript{35}.

In this work, taking into account the high abundance of Ni, Fe, Co, and Cu and they can easily form solid solutions with Pt. These transition metal elements are selected because their similar atomic radius and lower heat of formation make them likely to form stable HEAs\textsuperscript{20,28}. In addition, the DFT calculation provides a means to better understand the catalytic process and direct catalytic design\textsuperscript{13}. Based on this, we synthesized the small size (~3.4 nm) and uniform HEA Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27} nanoparticles (NPs) by a simple low-temperature oil phase synthesis method at atmospheric pressure. The Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27}/C catalyst displays a low overpotential (11 mV at 10 mA cm\textsuperscript{−2}), the activity of 10.96 A mg\textsuperscript{−1} at −0.07 V vs. reversible hydrogen electrode (RHE) for HER (reduction reaction) in 1 M KOH solution, and through the chronoamperometric tests and compared with commercial Pt/C. The Pt size (about 3.0 nm, Supplementary Fig. 4) on the Pt/C catalyst is similar to the size of HEA particles, so the electrocatalytic activity can be reasonably compared based on surface Pt sites. Figure 2a shows the CV curves of Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27}/C catalysts in N\textsubscript{2}-saturated 1 M KOH electrolyte, it also exhibited high mass activity (15.04 A mg\textsuperscript{−1}) and high selectivity and activity compared with traditional alloys\textsuperscript{13,26}. Moreover, the preparation of uniform nanostructured HEAs with small size (<10 nm) currently requires specific equipment (fast heating/cooling rate, ~10\textsuperscript{5} K per second), high temperature (~2000 kelvin), and high temperature resistant and conductive substrate (carbon nanofiber), such as carbon-thermal shock method\textsuperscript{35}.

In this work, taking into account the high abundance of Ni, Fe, Co, and Cu and they can easily form solid solutions with Pt. These transition metal elements are selected because their similar atomic radius and lower heat of formation make them likely to form stable HEAs\textsuperscript{20,28}. In addition, the DFT calculation provides a means to better understand the catalytic process and direct catalytic design\textsuperscript{13}. Based on this, we synthesized the small size (~3.4 nm) and uniform HEA Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27} nanoparticles (NPs) by a simple low-temperature oil phase synthesis method at atmospheric pressure. The Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27}/C catalyst displays a low overpotential (11 mV at 10 mA cm\textsuperscript{−2}), the activity of 10.96 A mg\textsuperscript{−1} at −0.07 V vs. reversible hydrogen electrode (RHE) for HER (reduction reaction) in 1 M KOH solution, and through the chronoamperometric tests and compared with commercial Pt/C. The Pt size (about 3.0 nm, Supplementary Fig. 4) on the Pt/C catalyst is similar to the size of HEA particles, so the electrocatalytic activity can be reasonably compared based on surface Pt sites. Figure 2a shows the CV curves of Pt\textsubscript{18}Ni\textsubscript{26}Fe\textsubscript{15}Co\textsubscript{14}Cu\textsubscript{27}/C catalysts in N\textsubscript{2}-saturated 1 M KOH electrolyte, it also exhibited high mass activity (15.04 A mg\textsuperscript{−1}) and high selectivity and activity compared with traditional alloys\textsuperscript{13,26}. Moreover, the preparation of uniform nanostructured HEAs with small size (<10 nm) currently requires specific equipment (fast heating/cooling rate, ~10\textsuperscript{5} K per second), high temperature (~2000 kelvin), and high temperature resistant and conductive substrate (carbon nanofiber), such as carbon-thermal shock method\textsuperscript{35}.
To better understand the HER performance of the Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C catalyst, we tested the electrochemical double-layer capacitance, electrochemical impedance spectra, and turnover frequency (TOF). We found that the electrochemical double-layer capacitance of Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C catalyst is higher than that of commercial Pt/C catalyst (Supplementary Fig. 5), indicating that the NPs-HEAs can expose more active sites. Also, electrochemical impedance spectra (Supplementary Fig. 6) exhibits Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C catalyst has a smaller semicircular diameter than commercial Pt/C catalyst, the transfer resistance of Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C is much lower than that of commercial Pt/C catalysts, indicating higher interfacial charge transfer rate and faster HER.
kinetics. The TOF value is used to characterize the activity of each site in the catalyst. It is found that the TOF value of the Pt18Ni26Fe15Co14Cu27/C catalyst is higher than Pt/C catalyst under various potentials (Supplementary Fig. 7), which shows the faster HER kinetics of Pt18Ni26Fe15Co14Cu27/C catalyst. These results further indicate that the NPs-HEAs can improve the catalytic activity effectively.

The stability of the catalysts was checked using the chronoamperometric method and 10,000th CV in 1 M KOH solution. The stability of the Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts were measured at an overpotential of 11 mV and 84 mV (under current density 10 mA cm⁻² condition, Supplementary Fig. 8), respectively. After 10 h test, 99% of the current density is maintained for the Pt18Ni26Fe15Co14Cu27/C catalyst, while the current density of the Pt/C catalyst is only kept about 53%. To further evaluate the stability of Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts, the 1000th and 10,000th CV cycles in 1 M KOH solution were performed. Figure 21 displays the LSV curves of Pt18Ni26Fe15Co14Cu27/C catalyst before and after 10000th and 10000th CV cycles. There is no obvious negative shift of the current density of 10 mA cm⁻², exhibiting higher stability than Pt/C catalyst (Supplementary Fig. 9, a negative shift of ~33 mV at 10 mA cm⁻² after 10,000th CV cycles). In addition, the morphology (Supplementary Fig. 10), the atomic ratio (Supplementary Table 1), lattice spacing and the XRD peaks (Supplementary Figs. 11) of catalyst do not change significantly after the stability test. In addition, the slight variations in the stoichiometry (Supplementary Table 2) after the electrocatalytic test was caused by the leaching of non-noble metals (Ni, Fe, Co, and Cu) in the catalyst. XPS analysis (Supplementary Fig. 12) shows that the Pt 4f, Ni 2p, Fe 2p, Co 2p, and Cu 2p spectra of Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts were very similar before and after electrocatalysis, while the oxide species increased slightly (Supplementary Table 3). However, the Pt/C catalyst shows obvious aggregation after the stability test (Supplementary Fig. 13). These results further suggest the excellent stability of the Pt18Ni26Fe15Co14Cu27/C catalyst.

Furthermore, taking the change of Cu element content as an example, the effect of stoichiometry variations on the electrocatalytic performance is discussed. Specifically, this synthesis method is used to prepare PtNiFeCoCu NPs with other Cu content (PtNiFeCoCu326 with slight stoichiometry variations, Pt12Ni32Fe25Co10Cu46 and Pt12Ni32Fe25Co10Cu46) by changing the amount of Cu precursor. From Supplementary Fig. 14, the morphology and size of the PtNiFeCoCu326, Pt12Ni32Fe25Co10Cu46 and Pt12Ni32Fe25Co10Cu46 NPs are similar to Pt18Ni26Fe15Co14Cu27 NPs. The PXRD pattern (Supplementary Fig. 15) suggests the fcc structure of the PtNiFeCoCu326, Pt12Ni32Fe25Co10Cu46 and Pt12Ni32Fe25Co10Cu46 NPs. The HER performance of PtNiFeCoCu326 catalyst with slight stoichiometry variations (Supplementary Figs. 16–24 and Supplementary Table 5) has no significant change compared with Pt18Ni26Fe15Co14Cu27/C (PtNiFeCoCu326/C). After activation (Supplementary Fig. 16), the PtNiFeCoCu326/C catalyst has close overpotential (11 mV, Supplementary Fig. 17a), area activity and mass activity (82.66 mA cm⁻² and 10.81 A mg⁻¹pt at ~0.07 V vs. RHE, Supplementary Fig. 17a–c), Tafel slope (30 mV dec⁻¹, Supplementary Fig. 18a), electrochemical double-layer capacitance (7.01 mF, Supplementary Fig. 19a, d), electrochemical impedance (Supplementary Fig. 20a), TOF value (Supplementary Fig. 21a, c) and stability (Supplementary Figs. 22–24) compared with PtNiFeCoCu326/C catalyst. In addition, the HER performance of Pt12Ni32Fe25Co10Cu46/C and Pt12Ni32Fe25Co10Cu46/C catalysts (Supplementary Figs. 16–24 and Supplementary Table 5) is slightly lower than the Pt18Ni26Fe15Co14Cu27/C catalyst. The order of activity is as follows: Pt18Ni26Fe15Co14Cu27/C (83.78 mA cm⁻² and 10.96 A mg⁻¹pt at ~0.07 V vs. RHE) = PtNiFeCoCu326/C (82.66 mA cm⁻² and 10.81 A mg⁻¹pt at ~0.07 V vs. RHE) > Pt12Ni32Fe25Co10Cu46/C (74.21 mA cm⁻² and 9.65 A mg⁻¹pt at ~0.07 V vs. RHE) > Pt12Ni32Fe25Co10Cu46/C (59.76 mA cm⁻² and 7.88 A mg⁻¹pt at ~0.07 V vs. RHE).

**Electrocatalytic performance tests toward MOR.** To further explore the Pt18Ni26Fe15Co14Cu27/C catalyst as redox bi-function electrocatalysts, we tested the MOR (oxidation reaction) activity. As shown in Fig. 3a and Supplementary Fig. 25, the Pt18Ni26Fe15Co14Cu27/C catalyst shows higher activity compared to Pt/C catalyst for MOR in 1 M KOH + 1 M CH₃OH electrolyte at a sweep rate of 20 mV s⁻¹. And an onset potential (the mass activity of 0.1 A mg⁻¹pt) was observed to decrease by 133 mV in the Pt18Ni26Fe15Co14Cu27/C catalyst compared to the Pt/C catalyst (the inset of Fig. 3a), indicating that the activation barrier of methanol oxidation is lower. The Pt18Ni26Fe15Co14Cu27/C catalyst achieves 10 times (4 times) higher in mass activity compared to Pt/C catalyst (15.04 A mg⁻¹, 114.93 mA cm⁻²) than that of Pt/C catalyst (1.45 A mg⁻¹, 17.48 mA cm⁻²) at peak potential for MOR (Fig. 3b). In addition, the MOR performance of PtNiFeCoCu326/C catalyst is similar to that of the Pt18Ni26Fe15Co14Cu27/C catalyst, the MOR performance of Pt12Ni32Fe25Co10Cu46/C and Pt12Ni32Fe25Co10Cu46/C catalysts is slightly lower than the Pt18Ni26Fe15Co14Cu27/C catalyst (Supplementary Fig. 26 and Supplementary Table 6). Moreover, among recently reported the Pt-based materials for MOR in alkaline medium, the Pt18Ni26Fe15Co14Cu27/C catalyst exhibits higher mass activity (Supplementary Table 8).

To study the stability of the Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts in MOR, the chronoamperometric test at 0.65 V vs. RHE and 1000 CV cycles were executed. After 5000 s chronoamperometric test (Fig. 3c), the Pt18Ni26Fe15Co14Cu27/C (3.79 A mg⁻¹pt) catalyst shows higher stability than that of commercial Pt/C (0.20 A mg⁻¹pt). After 1000 CV cycles, the mass activity of the Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts decay by about 6.4% and 26.9% (Fig. 3d and Supplementary Fig. 28a), further confirms the excellent stability of Pt18Ni26Fe15Co14Cu27/C catalyst. From Supplementary Figs. 27, 28, the order of catalysts stability is as follows: Pt18Ni26Fe15Co14Cu27/C > PtNiFeCoCu326/C > Pt12Ni32Fe25Co10Cu46/C > Pt12Ni32Fe25Co10Cu46/C > Pt12Ni32Fe25Co10Cu46/C. And the morphology and element ratio of PtNiFeCoCu/C catalyst with different rations did not obvious change after stability test (Supplementary Figs. 29, 30, Supplementary Table 1). However, the Pt/C catalyst shows obvious aggregation after the stability test (Supplementary Fig. 30d). XPS spectrum (Supplementary Fig. 31) shows that the Pt 4f, Ni 2p, Fe 2p, Co 2p, and Cu 2p spectra of Pt18Ni26Fe15Co14Cu27/C and Pt/C catalysts were very similar before and after MOR electrocatalysis. These test results indicate that the NPs-HEAs catalyst achieves double enhancement of catalytic activity and stability.

In MOR, the main route for catalyst deactivation is the poisoning effect of CO intermediates. To explore the poisoning effect of CO intermediates, the Iₚ/Iₜ (Iₚ: forward current density, Iₜ: backward current density) ratio of Pt18Ni26Fe15Co14Cu27/C catalyst (3.26) is larger than that of Pt/C (2.31), which shows the strong CO anti-poisoning performance of Pt18Ni26Fe15Co14Cu27/C catalyst. And from CO stripping curves (Supplementary Fig. 32), the onset potentials of the Pt18Ni26Fe15Co14Cu27/C (0.391 V vs. RHE) display a 181 mV decrease compared with Pt/C (0.572 V vs. RHE) catalyst. PtNiFeCoCu326/C (0.398 V vs. RHE), Pt12Ni32Fe25Co10Cu46/C (0.395 V vs. RHE), and Pt12Ni32Fe25Co10Cu46/C (0.413 V vs. RHE) catalysts have analogous onset potentials to Pt18Ni26Fe15Co14Cu27/C. It further shows that the PtNiFeCo/C catalyst has better CO anti-poisoning performance.
**Fig. 3** Methanol electro-oxidation performance of the Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C and Pt/C in 1 M KOH + 1 M CH$_3$OH electrolyte. **a** CV curves (the inset is the onset potential, the mass activity of 0.1 A mg$^{-1}$) of Pt/C and Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C. **b** Peak values of mass activity and area activity. **c** Chronoamperometric tests for MOR at 0.65 V vs. RHE. **d** CV curves of the Pt$_{18}$Ni$_{26}$Fe$_{15}$Co$_{14}$Cu$_{27}$/C before and after 1000 cycles.

**DFT studies.** We applied periodic DFT calculations to explore the HER and MOR performances in HEA. It is well known that the surface composition of the catalyst affects the catalytic performance. We use Ar$^+$ sputtering to study the change in surface element content of the PtNiFeCoCu NPs$^{[5]}$. After Ar$^+$ sputtering for 10 s, the relative content of the elements has been reduced, but the reduced contents of Ni, Cu, and Fe were slightly higher than that of Pt and Co (Supplementary Table 4). We have also compared the PDOS of the HEA with slightly different stoichiometry. As shown in Supplementary Fig. 33, the comparison models show the highly similar electronic structure with the models applied in the work, in which the peak positions and patterns of d orbitals in each element display very limited change. Therefore, the slight stoichiometry variations of the HEA will not significantly affect the electronic structure of the PDOS results. Based on this, after a detailed comparison of different random atomic arrangements, the HEA structure with slightly Ni and Cu enriched surface has been applied as the lattice model due to the highest stability (Fig. 4a). From the side view, the lattice has shown a highly stable structure, in which the lattice shows subtle distortion after relaxation, which indicates good durability for electrocatalysis. Meanwhile, the surface Ni and Co dominate the electroactive region near the Fermi level ($E_F$) (Fig. 4b). To further understand the electronic structure, the partial projected density of states (PDOS) of each element in HEA has been illustrated. Notably, Pt-5d occupies the deepest position near $E_F$ = −4.5 eV (EV = 0 eV), playing as the electron reservoir for the reduction process such as HER. Both Co-3d and Ni-3d orbitals dominate the bands near $E_F$, which locate at $E_F$ = 1.0 eV, contributing to the electron depletion center for HER and MOR. Moreover, the 3d orbitals of Cu, Co, and Fe not only alleviate the energy barrier of dual-way electron transfer for the oxidation and reduction process but also facilitate the stabilization of intermediates for MOR (Fig. 4c). A detailed study of the site-dependent PDOS of each element was illustrated (Fig. 4d). Notably, only the surface Pt demonstrates an evident upshift towards the $E_F$, which promotes the electron transfer for the HEA surfaces. Fe shows a site-independent electronic structure within HEA, which preserves the stable adsorption of intermediates with stronger anti-poisoning capability for the MOR process. From the bulk structure to the surface site, Co sites display an alleviation of the eg-t$_{2g}$ splitting, which promotes the enhanced electron transfer efficiency for electrocatalysis. Both Ni exhibits the relatively stable d-band-center to maintain the electroactive electron boosting center. For Cu sites closer to the surface, the 3d orbitals show a slight downshift trend to support the electroactivity of the HEA. Thus, the synergistic effect of multi-active sites on the HEA surface determines the remarkable performance of HER and MOR (Fig. 4d). For the HER process, the initial adsorption of water determines the efficiency of water-splitting and the following proton transfer. For the water adsorption process, the evident downshift of s,p orbitals of key intermediates has been noticed, which confirms the active electron transfer from the HEA to the water to achieve the stable adsorption and lays a good foundation for the following water dissociation (Fig. 4e). Similarly, we notice the adsorption of CH$_3$OH on HEA indicates the evident downshifting of s,p orbitals, and overlapping with electroactive d orbitals of the surface (Fig. 4f). For the multi-electron involved MOR process, the linear correlation of intermediates transformation is the key to guarantee the proton and electron transfer. Such a linear correlation is noticed for the s,p orbitals of key intermediates along the MOR process, which not only supports the efficient oxidation of the intermediates but also leads to the optimal binding strength during the intermediate transformation. Thus, superior MOR performance is guaranteed in the HEA (Fig. 4g).

Then, we further interpret the reaction trend for both HER and MOR from both the structural configuration and energetic reaction pathways. The most stable structural configurations of four key initial reactants and intermediates have been displayed.
The most stable adsorption of CH$_3$OH and H$_2$O locates near Ni and Fe sites, respectively. The OH is stabilized in the neighboring hollow sites, which avoids the active site blocking during both HER and MOR. Meanwhile, the H adsorption prefers the hollow site near Ni and Co, which is distinct from the OH. Thus, the multi-site adsorption for HER and MOR process on HEA guarantees superior performances (Fig.5a). Moreover, we have supplied the adsorption sites mapping of the surface to support the HER mechanism (Fig.5b). Notably, the different sites in HEA surfaces demonstrated very varied adsorption preference for the intermediates. For HER, the initial adsorption of H$_2$O locates on the Fe sites, which activates the dissociation of water molecules and facilitates the stabilization of $^*$OH in the neighboring hollow sites. Meanwhile, the nearby Ni, Co show the relatively preferred H$^*$ adsorption after the water dissociation, leading to the stabilization of H in the hollow sites surrounded by Co and Ni. The generated H$_2$ shows overall weak binding to the surface, indicating the quick desorption process to guarantee the efficient HER process. Therefore, our additional information has supplied the binding stability of the intermediates for the HER process, which supports the Volmer–Heyrovsky mechanism. The HER process supports a continuous downhill trend, confirming the efficient proton and electron transfer (Fig. 5c). Owing to the multi-active sites for OH and H, the water dissociation demonstrates a low activation barrier of 0.11 eV for the transition state (Fig. 5d). For the MOR process, the rate-determining step occurs at [CHO$^*$ + 3$^*$OH + 3H$_2$O] to [HCOOH + 2$^*$OH + 4H$_2$O] with the largest energy barrier of 0.45 eV. The transition state displays the activation energy of 0.64 eV. The overall MOR process is exothermic, which releases 2.34 eV energy (Fig.5e). The anti-poisoning capability is another essential requirement for the long-term application of MOR electrocatalysts. Compared to MOR, the formation of CO shows a much larger energy barrier of 0.81 eV and activation energy (0.94 eV), resulting in the suppression of the CO poisoning. The holistic reaction trend of the CO poisoning mechanism is also much weaker than the MOR process, which explains both the superior electroactivity and durability of the HEA (Fig. 5f).
Discussion

In summary, we have synthesized the uniform and small size Pt_{18}Ni_{26}Fe_{15}Co_{14}Cu_{27} NPs HEA nanoparticles by a simple low-temperature synthesis method at atmospheric pressure. Electrocatalytic test results showed that the obtained Pt_{18}Ni_{26}Fe_{15}Co_{14}Cu_{27}/C catalyst has excellent bi-functional electrocatalytic properties for reduction reaction (HER) and oxidation reaction (MOR). Pt_{18}Ni_{26}Fe_{15}Co_{14}Cu_{27}/C catalyst showed an ultrasmall overpotential (11 mV at 10 mA cm\(^{-2}\)) and superior activity (10.96 A mg\(^{-1}\)) and stability for HER, which is one of the best HER activity in alkaline medium. And it is also the effective catalysts for MOR and displayed the excellent activity (15.04 A mg\(^{-1}\)) and better CO anti-poisoning in alkaline solution, which is the best alkaline MOR activity among the ever reported. Through DFT calculations, the origin of remarkable electroactivity and durability of HEA in HER and MOR is attributed to the synergistic effect of each element for efficient electron transfer. The suitable electronic environment of the HEA realizes the multi-active sites for appropriate adsorption of key intermediates and efficient electron transfer during the electrocatalysis, which maximizes the utilization of surface electroactivity. The simple oil phase synthesis strategy proposed in this work, as well as the multi-active sites and fast site-to-site electron transfer mechanism, which is expected to lay the foundation for the preparation of other HEAs and their application in related electrocatalysis.

Methods

Materials. Platinum (II) acetylacetonate (Pt(acac)\(_2\), 97%), nickel (II) acetylacetonate (Ni(acac)\(_2\), 95%), Molybdenum hexacarbonyl (Mo(CO)\(_6\), 98%), oleylamine (OAm, >70%) and glucose were bought from Sigma-Aldrich. Cupric acetylacetonate (Cu(acac)\(_2\), 98%) was purchased from Energy Chemical. (1-Hexadecyl) trimethylammonium chloride (CTAC, 96%), Tris(2,4-pentanedionato) Cobalt (III) (Co(acac)\(_3\), 98%), Iron (II) 2,4-pentanedionate (Fe(acac)\(_2\), 98%) and Nafion solution (5 wt.%) were supplied by Alfa Aesar. Methanol, cyclohexane, ethanol, and isopropanol were bought from Beijing Tongguang Fine Chemicals Company. Potassium hydroxide (KOH, 90%) was purchased from Aladdin.

Preparation of HEA Pt\(_{18}\)Ni\(_{26}\)Fe\(_{15}\)Co\(_{14}\)Cu\(_{27}\) NPs. CTAC (50 mg) was added into oleylamine (5 mL) in a 15 mL vial. After sonication for about 15 min, Pt(acac)\(_2\) (10 mg), Ni(acac)\(_2\) (6.4 mg), Fe(acac)\(_2\) (8.8 mg), Co(acac)\(_3\) (8.9 mg), Cu(acac)\(_2\) (6.5 mg), glucose (60 mg), and Mo(CO)\(_6\) (33 mg) were added into the vial. In order to obtain a homogeneous solution, the mixture was sonicated for 1 h. The vial was heated to 220 °C at 5 °C min\(^{-1}\) and then kept 2 h under magnetic stirring at 400 rpm. The black colloidal products were collected by centrifugation and washed two times with an ethanol/cyclohexane mixture. Finally, the black colloidal products were kept in cyclohexane for further use.

Preparation of alloy PNiFeCoCu with different element ratios NPs. CTAC (50 mg) was added into oleylamine (5 mL) in a 15 mL vial. After sonication for about 15 min, Pt(acac)\(_2\) (10 mg), Ni(acac)\(_2\) (6.4 mg), Fe(acac)\(_2\) (8.8 mg), Cu(acac)\(_2\) (6.5 mg), glucose (60 mg), and Mo(CO)\(_6\) (33 mg) were added into the vial. In order to obtain a homogeneous solution, the mixture was sonicated for 1 h. The vial was heated to 220 °C at 5 °C min\(^{-1}\) and then kept 2 h under magnetic stirring at 400 rpm. The black colloidal products were collected by centrifugation and washed two times with an ethanol/cyclohexane mixture. Finally, the black colloidal products were kept in cyclohexane for further use.
Preparation of PtNiFeCoCu/C. The obtained 1 mg HEA NPs dispersed in 10 mL cyclohexane was mixed with 4 mg of carbon (Ketjen Black-300) in 10 mL ethanol under sonication for 1 h, and then the product was collected via centrifugation with ethanol. The PtNiFeCoCu/C catalysts were further cleaned (remove organic spec- ies) with 0.5 M acetic acid (ethanol solution) under N2 atmosphere. After being sonicated for 2 h, the products were collected by centrifugation and washed with ethanol for three times.

Characterization. The TEM and high-resolution TEM (HRTEM) images of the samples were characterized by an FEI Tecnai-G2 F30 at an accelerating voltage of 300 kV. Powder X-ray diffraction (XRD) spectra were recorded on X’Pert-PRO MPD diffractometer operating at 40 kV and 40 mA with Cu Ka radiation. The compositions of the HEA NPs were determined by the inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian 710-ES). The catalysts after the durability tests were scratched off the glassy carbon electrode with the aid of sonication in ethanol and then collected for further TEM, XRD, and ICP char- acterization. Ten microliters of the catalysts were dropped onto the GCE surface as a reference catalyst for electrochemical tests under the same conditions. And 1000th/10000th CVs were also measured to evaluate the stability of catalysts. Finally, the black colloidal products were kept in cyclohexane for further use. The synthesis of NPs with other element ratios only changes the amount of Cu (acac)2 precursor (4.0 mg and 8.5 mg).

Electrochemical measurements. The 1 mg PtNiFeCoCu/C catalysts were dispersed in a mixture of 495 µL ultrapure water, 495 µL isopropanol, and 10 µL Naion solution, after sonication for 1 h, PtNiFeCoCu/C catalyst with the con- centration of 1 mg mL⁻¹ was obtained.

Electrochemical measurements were conducted on a CHI 760E Electrochemical Workstation (Shanghai Chenhua Instrument Corporation, China) in a conventional three-electrode cell. The graphite rod electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was a glassy carbon electrode (GCE, diameter: 3 mm, area: 0.07065 cm²). Ten microliters of the catalyst were dropped onto the GCE surface for further electrochemical tests. All the potentials reported in this work were considered based on the intermediate adsorptions on the surface.

Hydrogen evolution reaction (HER) measurements. The HER performance of the catalysts was evaluated by linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹ in N₂-saturated 1 M KOH solution, and all polarization curves were 95% iR-corrected. The durability tests were performed in 1.0 M KOH solution using the chronoamperometric method. And 1000th/10000th CVs were also measured to evaluate the stability of catalysts. 20% Pt/C catalyst was also dropped on the GCE as a reference catalyst for electrochemical tests under the same conditions.

TOF calculation. The CVs curve was collected from 0 to 1.2 V vs. RHE in 0.5 M H₂SO₄ solution with a scan rate of 20 mV s⁻¹:

\[ n = \frac{Q_{\text{ox}}}{2F} \]  

\[ \text{TOF (s}^{-1}) = \frac{1}{2FQ/n} \]  

where \( n \) is the number of active sites, number 2 represents two electrons (produce one hydrogen molecule), \( Q \) represents electron transfer quantity (the hydrogen desorption peak), \( F \) is Faraday’s constant (96483.3 C mol⁻¹), and \( (A) \) is the current measured at a specific potential during LSV measurement.

Methanol oxidation reaction (MOR) measurements. The CVs for MOR were conducted in N₂-saturated 1 M KOH + 1 M CH₃OH solution between 0.2–1.2 V vs. RHE with a scan rate of 20 mV s⁻¹. For the MOR stability tests, chronoamperometric tests were performed at a fixed potential of 0.65 V vs. RHE, and 1000th CVs were also performed to evaluate the stability of catalysts.

CO stripping curves were carried out in 1 M KOH solution. Before the tests, 1 M KOH solution was first deaerated with high-purity N₂. Then, CO was bubbled into the cell for 15 min while the potential of the working electrode was held at a constant potential of 0.1 V vs. RHE. Then N₂ was bubbled into the system for 15 min to remove CO gas. After that, CO stripping curves were recorded between 0 and 1.2 V vs. RHE at a scan rate of 20 mV s⁻¹.

Calculation setup. For all the calculations within this work, we have applied the DFT calculations within CASTEP code. The GGA and PBE exchange-correlation functionals are selected for all the calculations. The cutoff energy of plane-wave basis sets based on the ultrasoft pseudopotential has been set to 4.0 eV with the same settings of the algorithm total energy for all the geometry optimizations. To specifically discuss the electrocatalysis on the surface, we have applied the HEA model with similar stoichiometry as experimental characterizations. The HEA model has been built, which consists of 126 atoms in total. The atomic arrangements of different elements are constructed randomly by following the same ratio as the experiments of PtₓNiₓFeₓCoₓCuₓ/Cₓ. Based on the components of the HEA by experimental characterizations, Ni and Cu have the highest concentration, which is 26% and 27%, respectively. To determine the most possible preferred model, we have compared the total energy of the HEA model with different surface arrangements, in which the present applied model with Cu and Ni slight rich feature has been the most stable one. Therefore, we have applied the HEA surface model with Cu and Ni rich feature. The reaction energy has been considered based on the intermediate adsorptions on the surface.

The Monkhost–Pack reciprocal space integration was performed using coarse k-points with a mesh of 2 × 2 × 1 k, which was guided by the initial convergence test. With these settings, the overall total energy for each step is converged to less than 5.0 × 10⁻⁵ eV per atom. The Hellmann-Feynman forces on the atom were converged to less than 0.001 eV Å⁻¹.

Data availability

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

Code availability

All code supporting the findings of this study are available from the corresponding author on request.

Received: 23 July 2020; Accepted: 6 October 2020; Published online: 28 October 2020

References

1. Glenk, G. & Reichelstein, S. Economics of converting renewable power to hydrogen. *Nature Energy* **4**, 216–222 (2019).

2. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **355**, 146–157 (2017).

3. Lai, J. & Guo, S. Design of ultrathin Pt-based multilayer nanostructures for efficient oxygen reduction electrocatalysis. *Small* **13**, 1702156 (2017).

4. Yin, H. et al. 2D Electro catalysts for converting earth-abundant simple molecules into value-added commodity chemicals: recent progress and perspectives. *Adv. Mater.* **32**, 1904870 (2019).

5. Lewo, R. et al. Chloride-mediated selective electrosynthesis of ethylene and propylene oxides at high current density. *Science* **368**, 1228 (2020).

6. Li, L., Wang, P., Shao, Q. & Huang, X. Metallic nanostructures with low dimensionality for electrochemical water splitting. *Chem. Soc. Rev.* **49**, 3072–3106 (2020).

7. Lai, J., Nasibamina, A., Luque, R. & Xu, G. 3D porous carbonaceous electrodes for electrocatalytic applications. *J. Mater. Chem. A* **6**, 76–81 (2018).

8. Xie, C. et al. Insight into the design of defect electrocatalysts: from electronic structure to adsorption energy. *Mater. Today* **31**, 47–68 (2019).

9. Jin, H. et al. Emerging two-dimensional nanomaterials for electrocatalysis. *Chem. Rev.* **118**, 6337–6408 (2018).

10. Chen, Y. et al. Phase engineering of nanomaterials. *Nat. Rev. Chem.* **4**, 234–236 (2020).

11. Tian, X., Lu, X. F., Xia, B. Y. & Lou, X. W. Advanced electrocatalysts for the oxygen reduction reaction in energy conversion technologies. *Joule* **4**, 45–68 (2020).

12. Yuan, Y. et al. Zirconium nitride catalysts surpass platinum for oxygen reduction. *Nat. Mater.* **19**, 282–286 (2020).

13. Batchelor, T. A. A. et al. High-entropy alloys as a discovery platform for electrocatalysis. *Joule* **3**, 834–845 (2019).

14. George, E. P., Raabe, D. & Ritchie, R. O. High-entropy alloys. *Nat. Rev. Mater.* **4**, 515–534 (2019).
15. Chen, P. C. et al. Polyelemental nanoparticle libraries. *Science* **352**, 1565–1569 (2016).

16. Koo, W. T., Millstone, J. E., Weiss, P. S. & Kim, I. D. The design and science of polyelemental nanoparticles. *ACS Nano* **14**, 6407–6413 (2020).

17. Miracle, D. R. & Senkov, O. N. A critical review of high entropy alloys and related concepts. *Acta Mater.* **122**, 448–511 (2017).

18. Huang, K. et al. Exploring the impact of atomic lattice deformation on oxygen evolution reactions based on a sub-5 nm pure face-centred cubic high-entropy alloy electrocatalyst. *J. Mater. Chem. A* **6**, 11938–11947 (2020).

19. Lei, Z. et al. Enhanced strength and ductility in a high-entropy alloy via ordered oxygen complexes. *Nature* **563**, 546–550 (2018).

20. Zhang, W., Liaw, P. K. & Zhang, Y. Science and technology in high-entropy alloys. *Sci. China Mater.* **61**, 2–22 (2018).

21. Yeh, J. W. et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv. Eng. Mater.* **6**, 299–303 (2004).

22. Guo, C. et al. Intermediate modulation on noble metal hybridized to 2D metal-organic framework for accelerated water electrolysis. *Chem* **5**, 2429–2441 (2019).

23. Lu, F. et al. Ir-led alloy nanoflowers with optimized hydrogen binding energy as bifunctional electrocatalysts for overall water splitting. *Small Methods* **4**, 1900129 (2020).

24. Tian, X. et al. Engineering bunched Pt–Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. *Science* **366**, 850–856 (2019).

25. Xiong, L. et al. Octahedral gold-silver nanoframes with rich crystalline defects for efficient methanol oxidation manifesting a CO-promoting effect. *Nat. Commun.* **10**, 3782 (2019).

26. Zhang, G. et al. High entropy alloy as a highly active and stable electrocatalyst for hydrogen evolution reaction. *Electrochim. Acta* **279**, 19–23 (2018).

27. Glasscott, M. W. et al. Electrolysis of hydrogen-rich metallic glass nanoparticles for designer, multi-functional electrocatalysts. *Nat. Commun.* **10**, 2650 (2019).

28. Jin, Z. et al. Nanoporous Al–Ni–Co–Ir–Mo high-entropy alloy for record-high water splitting activity in acidic environments. *Small* **15**, 1904180 (2019).

29. Qiu, H. J. et al. Nanoporous high entropy alloys for highly stable and efficient electrocatalysts. *J. Mater. Chem. A* **7**, 6499–6506 (2019).

30. Xie, Y. W. et al. Highly efficient decomposition of ammonia using high-entropy alloy catalysts. *Nat. Commun.* **10**, 4011 (2019).

31. Yao, C. Z. et al. Electrochemical preparation and magnetic study of Bi–Fe–Co–Ni–Mn high entropy alloy. *Electrochim. Acta* **53**, 8339–8365 (2008).

32. Soare, V. et al. Electrochemical deposition and microstructural characterization of AlCrFeMnNi and AlCrCuFeMnNi high entropy alloy thin films. *Appl. Surf. Sci.* **358**, 533–539 (2015).

33. Nellaiappan, S. et al. High-entropy alloys as catalysts for the CO2 and CO reduction reactions: Experimental realization. *ACS Catal.* **10**, 3658–3663 (2020).

34. Pedersen, J. K., Batchelor, T. A. A., Bagger, A. & Rossmeisl, J. High-entropy alloys as catalysts for the CO2 and CO reduction reactions. *ACS Catal.* **10**, 2169–2176 (2020).

35. Yao, Y. et al. Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science* **359**, 1489–1494 (2018).

36. Luo, X. et al. Spin regulation on 2D Pd–Fe–Pt nanomeshes promotes fuel electrooxidations. *Nano Lett.* **20**, 1967–1973 (2020).

37. Xie, Y. et al. Boosting water dissociation kinetics on Pt–Ni nanowires by N-induced orbital tuning. *Adv. Mater.* **31**, 1807780 (2019).

38. Li, T. et al. Galvanic replacement mediated 3D porous PtCu nano-frames for enhanced ethylene glycol oxidation. *Chem. Commun.* **55**, 14526–14529 (2019).

39. Ding, J., Shao, Q., Feng, Y. & Huang, X. Ruthenium-nickel sandwiched nanofilms for efficient water splitting electrocatalysis. *Nano Energy* **47**, 1–7 (2018).

40. Li, H. et al. Surface oxygen-mediated ultrathin PtRuM (Ni, Fe, and Co) nanowires boosting methanol oxidation reaction. *J. Mater. Chem. A* **8**, 2323–2330 (2020).

41. Chen, L. et al. Improved ethanol electrooxidation performance by shortening Pd-Ni active site distance in Pd–Ni–P nanocatalysts. *Nat. Commun.* **8**, 14136 (2017).

42. Huang, W. et al. Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum-nickel hydroxide-graphene. *Nat. Commun.* **6**, 10035 (2015).

43. You, B. et al. Universal surface engineering of transition metals for superior electrocatalytic hydrogen evolution in neutral water. *J. Am. Chem. Soc.* **139**, 12283–12290 (2017).

44. Stewart, J. C. et al. First principles methods using CASTEP. *Kist-Cryst. Mater.* **220**, 567–570 (2005).

45. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).

46. Perdew, J. P. et al. Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **46**, 6671–6687 (1992).

47. Head, J. D. & Zerner, M. C. A Broyden–Fletcher–Goldfarb–Shanno optimization procedure for molecular geometries. *Chem. Phys. Lett.* **122**, 264–270 (1985).

48. Probert, M. J. I. & Payne, M. C. Improving the convergence of defect calculations in supercells: An ab initio study of the neutral silicon vacancy. *Phys. Rev. B* **67**, 075204 (2003).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21571112, 51572136, 51772162, 51802171), the Taishan Scholars Program, National Science Foundation of Shandong Province, China (ZR2018RFB031), Open Fund of the Key Laboratory of Eco-chemical Engineering (Qingdao University of Science and Technology, No. RF1702), the Taishan Scholar Project of Shandong Province (tq201909123).

Author contributions

L.W. and J.L. conceived and supervised the research. J.L. and H.L. designed the experiments. H.L. performed most of the experiments and data analysis. B.H. performed the DFT calculations and mechanistic analysis. Y.H. and H.Z. prepared the electrodes and helped with electrochemical measurements. W.Q. and D.Z. conducted and analyzed HRTEM micrographs and mapping images. Y.Y. performed and analyzed XRD and ICP measurements. S.L. and W.C. analyzed XPS measurements. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-19277-9.

Correspondence and requests for materials should be addressed to J.L., B.H. or L.W.

Peer review information *Nature Communications* thanks Jan Philipp Hofmann, Frederik Tielens and other, anonymous, reviewers for their contributions to the peer review of this work. Peer review reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2020