Trimetallic TriStar Nanostructures: Tuning Electronic and Surface Structures for Enhanced Electrocatalytic Hydrogen Evolution

Nana Du, Chengming Wang, Xijun Wang, Yue Lin, Jun Jiang, and Yujie Xiong*

Despite the rapid development on alternative materials, Pt is still the most efficient material for various electrocatalytic reactions. To lower the material cost and tune the electrocatalytic performance, there is a major trend to develop Pt-based alloy materials through various synthetic methods. Among the alloy materials, late transition metals such as Fe and Co are popularly used to form highly electrocatalytically active alloys with Pt. Motivated by this success, great efforts have been made to examine the roles of transition metals in the performance improvement.

Theoretical simulations have predicted that the incorporated transition metals can tune adsorption energies, blocking species coverage and surface electronic structure (i.e., d-band center) toward optimal electrocatalytic activity. The past research indicates that each transition metal may exhibit a specific function in manipulating the behavior of Pt-based alloy materials in electrocatalytic reactions. For this reason, it can be anticipated that building more complex alloy lattices, which moves from bimetallic alloys (e.g., PtFe and PtCo) forward to trimetallic systems (e.g., PtFeCo), would open the possibility of further enhancing the electrocatalytic activity. In this case, the compositions of trimetallic alloys absolutely matter to their overall performance. To this end, it requires a library of samples with tunable compositions to provide a platform for establishing the relationship between compositions and electrocatalytic performance. Despite this demand by fundamental research, no synthesis has yet been reported, to the best of our knowledge, for the PtFeCo alloy nanostructures with tunable compositions.

In addition to the compositions, electrocatalytic reactions are very structure-sensitive like other catalytic systems, which makes the surface structures of Pt-based electrocatalysts a versatile knob for tuning their activities. Thus one can combine composition engineering with surface structure control to boost the performance of alloy electrocatalysts. In recent years, particular attention has been paid on electrocatalytic hydrogen evolution reaction (HER, $2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$), a highly important process for hydrogen generation to constitute reversible hydrogen fuel cell technology. In this communication, we for the first time report the synthesis of PtFeCo alloy nanostructures in a TriStar shape with tunable Fe and Co contents toward the HER application. It turns out that the incorporation of Co into PtFe alloys tunes charge density and surface electronic structure while the TriStar shape enables highly active surface for the reaction, allowing tuning the overall HER performance.

We first assess the effects of Fe and Co on the HER performance of Pt-based alloys by benchmarking Pt$_{81}$Fe$_{29}$Co$_6$ nanoparticles (namely, PtFeCo NP, Figures S1 and S2 in the Supporting Information) against Pt$_{81}$Fe$_{33}$ and Pt$_{81}$Co$_{34}$ nanoparticles (namely, PtFe NP and PtCo NP, Figure S3 in the Supporting Information) with an approximately comparable ratio of Pt to Fe/Co. The trimetallic PtFeCo NP sample is synthesized via an organic-phase process, in which platinum (II) acetylacetonate (Pt(acac)$_2$), iron (III) nitrate (Fe(NO$_3$)$_3$), and cobalt (II) acetylacetonate (Co(acac)$_2$) in 1-octadecene (ODE) are co-reduced by 1,2-tetradecanediol (TDD) in the presence of oleylamine (OLA), oleic acid (OA), and 1-dodecanethiol (DDT). Specifically, the OLA and OA serve as stabilizing agents whose ratio determines nucleation and growth rates, while the DDT is utilized as a coordination chemical to balance the reduction rates of Pt, Fe, and Co precursors. The PtFe NP and PtCo NP are prepared as reference samples by following the established protocols in the literature.

Figure S4 (Supporting Information) shows the HER performance of the three Pt-based alloy NP samples. PtFe NP exhibits slightly higher activity than PtCo NP in terms of current densities. Interestingly, trimetallic PtFeCo NP shows the dramatically enhanced HER performance in comparison with the bimetallic nanoparticles. Our previous research has suggested that the interfacial polarization between Pt and the other metal with lower work function may induce the accumulation of negative charges on Pt surface and facilitate the HER process. To acquire the situation in the present case, we calculate the charge densities of Pt and Fe or Co atoms in a Pt$_{81}$(Fe/Co)$_{27}$ alloy lattice (see Table S1, Supporting Information) by first-principles simulations. It demonstrates that the Fe can induce more significant charge polarization on Pt than the case of PtCo in either neutral state or with the addition of extra electrons (that roughly represents the working condition of electrocatalysis), which will explain the high HER activity of PtFe NP. When one Fe atom in the Pt$_{81}$Fe$_{27}$ lattice is replaced...
by Co (Figure S5, Supporting Information), the total charge accumulation on the 81 Pt atoms is slightly reduced. However, the Pt atoms close to the Co ($d = 2.73$ and $4.73$ Å) would accumulate the increased numbers of electrons, generating highly active sites. On the other hand, the electron accumulation on the long-distance sites ($d = 8.20$ and $9.07$ Å) is diminished. For this reason, it is necessary to incorporate sufficient numbers of Co atoms into the PtFe lattice, providing more active sites.

In addition to the composition engineering, the HER performance can also be maneuvered by the control of surface structure through the synthesis of PtFeCo alloy nanostructures in a TriStar shape. The only difference between this synthesis and that for PtFeCo NP is the addition of tetraoctylammonium bromide (TOAB). TOAB is an effective capping agent for Pt,[22–24] and as a result, the surface structure of Pt-based alloy nanoparticles can be controlled. Figure 1a shows the transmission electron microscope (TEM) image of the obtained Pt$_{81}$Fe$_{29}$Co$_{6}$ nanostructures that have the same compositions as the PtFeCo NP. The nanostructures exhibit a TriStar shape (namely, PtFeCo TriStar 1), and have a branch length of $\approx 12$ nm and diameter of $\approx 4$ nm.

The structure of TriStar is further characterized by high-resolution TEM (HRTEM). As shown in Figure 1b, the observed lattice fringes can be assigned to the forbidden $1/3\{422\}$ reflection indicating the existence of a layer of twin plane in between.[28] It indicates that the top and bottom surfaces of TriStar are the $\{422\}$, which are less closely packed than low-index facets. The growth axis of each branch is determined to $\{211\}$, and the edges of branches contain abundant stepped atoms (as marked by the $\{100\}$ and $\{111\}$ stepped facets), which is consistent with the previously reported Pt tripods.[16,29,30] This observation also indicates that the growth of PtFeCo alloy TriStar is mainly driven by the component of Pt in which TOAB, the capping agent for Pt, can play a key role. Scanning TEM (STEM) and energy-dispersive spectroscopy (EDS) mapping analyses in Figure 1c–f further confirm the TriStar shape and uniform distribution of elements.

The surface structure having the low-coordinated stepped atoms on edges as well as the loosely-packed $\{422\}$ top and bottom surfaces can provide highly active sites for reactions, opening up the possibility of further improving the HER activity of PtFeCo nanoparticles. Figure S6 (Supporting Information) compares the HER performance of PtFeCo TriStar 1 with PtFeCo NP in terms of current densities. Despite the same compositions, the PtFeCo TriStar 1 sample exhibits remarkably higher activity than the PtFeCo NP owing to its unique surface structure. The surface structure effect can also be appreciated from the HER performance comparison (Figure S7, Supporting Information) of PtFe NP with PtFe TriStar (see the morphology in Figure S8, Supporting Information).

The surface structures of the TriStar samples contribute to the HER performance enhancement from two aspects. The blank CV curves in Figure S9a (Supporting Information) show that the TriStar sample has larger electrochemical surface area than the nanoparticles with the similar chemical composition, suggesting that the TriStar structure provides more active sites.
for HER. Another contribution from the TriStar structure is the relatively flat surface that makes the sample have better contact with the electrode. We have performed electrochemical impedance spectroscopy (EIS) on the electrodes modified by TriStar and nanoparticle samples. With the similar chemical compositions, the contact resistance between TriStar and electrode is significantly lower than that by nanoparticles. Taken together, this unique shape can boost the efficiency of HER reaction.

As an indicator for the rate-determining reactions, the Tafel slope has also been analyzed. Although the rate-determining steps may not be so well represented when overpotential is relatively small, the relevance of Tafel slopes to alloy compositions can still provide an assessment reference for HER studies in addition to current densities. The PtFe NP and PtFe TriStar have very close Tafel slopes (Figure S7b, Supporting Information), and the Tafel slope of PtFeCo NP is comparable to that of PtFeCo TriStar 1 as well (see Figure S6b, Supporting Information). It suggests that the control over surface structure does not have a distinct effect on the reaction process. On the other hand, by incorporating Co into PtFe lattice, both the TriStar and NP samples exhibit the reduced Tafel slopes. This finding in agreement with the trend of current densities indicates that the composition engineering can tune the reaction process.

Our synthetic method for TriStar nanostructures offers the capability of tuning the compositions by altering the doses of chemical agents and reaction temperatures (see the synthetic conditions in Table S2 in the Supporting Information). The chemical compositions are measured by inductively-coupled plasma mass spectrometry (ICP-MS), which reveals that the samples marked as TriStar 2 (Figure S10, Supporting Information), TriStar 3 (Figure 2), and TriStar 4 (Figure S11, Supporting Information) have the compositions of Pt$_{81}$Fe$_{28}$Co$_{8}$, Pt$_{81}$Fe$_{28}$Co$_{10}$, and Pt$_{81}$Fe$_{27}$Co$_{13}$, respectively, with the ratio of Co to Fe gradually increased. We have further employed X-ray diffraction (XRD) to characterize the samples. As indicated by Figure S12 (Supporting Information), all the peaks that gradually shift toward higher angles with the increase of Co content can be indexed to the face-centered cubic (fcc) structure. Specifically, the lattice constants ($a$) that are determined by the XRD diffraction peaks agree with those calculated from the compositions based on the standard JCPDS diffraction data (Pt, 04–0802; Pt$_3$Fe, 29–0716; Pt$_3$Co, 29–0499) (see Table 1). It well demonstrates the alloy nature of samples. Despite their tunable compositions, all the samples share the same TriStar shape and surface structure, providing a platform for investigating the composition-dependent HER performance.

Figure 3a outlines the polarization curves of the current density plotted against potential for all the TriStar-shaped samples, with the commercially available Pt/C catalyst as a reference sample. The current densities at the same potential are found to be in the order of PtFe TriStar $<$ PtFeCo TriStar 1 $<$ PtFeCo TriStar 2 $<$ PtFeCo TriStar 3 $>$ PtFeCo TriStar 4 with the increase of Co contents, all of which significantly exceed that of Pt/C. Among the samples, the PtFeCo TriStar 3 with the medium ratio of Co to Fe shows the highest activity.
with an extremely large current density of 1325 mA cm\(^{-2}\) at potential of \(-400\) mV. To decode the mechanism for this current density–composition relationship, we have collected blank CV curves and EIS Nyquist plots (Figure S14, Supporting Information), which reflects the electrochemical surface areas and conductivities of samples, respectively. The data suggest that the variation in Fe and Co chemical compositions has little impact on the conductivities and electrochemical surface areas. Thus, the tunable current densities by composition control should be related to the reaction process occurring at the catalyst surface.

Meanwhile, the trend of HER performance is reflected by the corresponding Tafel plots (Figure 3b). The Tafel slopes vary from 30 to 21 mV decade\(^{-1}\), and are in inverse order to the current densities. This trend, as a reference in addition to the current density assessment, also demonstrates that the HER performance can be tuned by tailoring the ratio of Co to Fe in the alloy lattices. The Tafel slopes below 30 mV decade\(^{-1}\) have been previously reported for some different cases of Pt-based alloys.\(^{32–35}\) Note that the HER reaction occurring on Pt electrode includes underpotential hydrogen adsorption whose potential range is between 0.05 and 0.4 V. For this reason, the

Table 1. Chemical compositions of the samples determined by ICP-MS and their (200) diffraction peak positions recorded on XRD. The lattice constants (\(a\)) can be calculated from the XRD (200) diffraction or from the chemical compositions based on the standard JCPDS data (Pt, 04–0802; Pt\(_3\)Fe, 29–0716; Pt\(_3\)Co, 29–0499). The XRD patterns are shown in Figures S2 and S11 (Supporting Information).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt:Fe:Co atomic ratio by ICP-MS</th>
<th>Lattice (a) value calculated by compositions [Å]</th>
<th>XRD (200) diffraction peak position [°]</th>
<th>Lattice (a) value calculated by XRD [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtFe TriStar</td>
<td>81:32</td>
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<td>47.138</td>
<td>3.857</td>
</tr>
<tr>
<td>PtFeCo NP</td>
<td>81:29:6</td>
<td>3.847</td>
<td>47.208</td>
<td>3.852</td>
</tr>
<tr>
<td>PtFeCo TriStar 1</td>
<td>81:29:6</td>
<td>3.847</td>
<td>47.177</td>
<td>3.854</td>
</tr>
<tr>
<td>PtFeCo TriStar 2</td>
<td>81:28:8</td>
<td>3.841</td>
<td>47.361</td>
<td>3.841</td>
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<tr>
<td>PtFeCo TriStar 3</td>
<td>81:28:10</td>
<td>3.837</td>
<td>47.411</td>
<td>3.837</td>
</tr>
<tr>
<td>PtFeCo TriStar 4</td>
<td>81:27:13</td>
<td>3.830</td>
<td>47.545</td>
<td>3.828</td>
</tr>
</tbody>
</table>

Figure 3. a) Polarization curves obtained on glassy carbon rotating disk electrodes deposited with Pt-based alloy TriStar nanostructures in different chemical compositions in reference to Pt/C at the same total metal loading weights in a 0.5 M H\(_2\)SO\(_4\) (aq) electrolyte. b) The corresponding Tafel plots. The dashed lines indicate the linear regions. Durability tests for the c) Pt/C and d) PtFeCo TriStar 3 sample.
negative currents originating from underpotential hydrogen adsorption can possibly arise above 0 V in the sweep from 0.1 to −0.4 V, particularly when the charge density and d-band center are altered in the Pt-based alloy system. The negative currents above 0 V make the value of overpotential appear a negative number in Tafel plots. The negative currents above 0 V have also been previously reported for alloy HER in literature. [11] The electrochemical stability of the samples, another important parameter is also assessed by running continuous cyclic voltammetry curves (CVs) between −0.4 and 0.1 V versus RHE at 50 mV s⁻¹. While the Pt/C shows relatively weak stability (Figure 3c), negligible decay in the HER activity can be observed for the PtFeCo TriStar 3 between the curves measured at the initial cycle and after 5000 CV cycles (Figure 3d). It demonstrates the excellent durability of our samples during long-term cycling. As indicated by ICP-MS measurements, the composition of the PtFeCo TriStar 3 is only slightly changed from Pt₈₁Fe₂₂Co₅ to Pt₈₁Fe₂₀Co₇ after the 5000 cycle durability test, indicating the high resistance to etching in acid. TEM, HRTEM, and STEM analyses in Figure S13 (Supporting Information) also show that the morphology and surface structure of the TriStar sample are largely maintained after the HER reaction, which can be responsible for the excellent durability.

Upon assessing the HER performance, a question naturally arises: what factor makes the HER activity so dependent on the ratio of Co to Fe in Pt-based alloys? Since the dependence seems to be more related to the reaction process, it would be valuable to provide the information for intrinsic electronic structures.[10] We have performed theoretical simulations to analyze the effect of chemical compositions on electronic structures. To reflect the varied compositions, we first calculate the Bader charge increase on the Pt atoms in three alloy models (Pt₈₁Fe₂₂Co₅, Pt₈₁Fe₂₀Co₇, and Pt₈₁Fe₁₈Co₉ as in Figure 4a–c) in relative to the Pt in Pt₈₁Fe₂₇. The three alloy models have the Co:Fe ratios from 5:22 up to 1:2, nearly covering the composition range of our samples. In the simulations, in order to have various atoms uniformly distributed in an atomic model, the atomic ratios are not exactly the same as those for our synthesized samples. As indicated by Figure 4d and Figure S15 (Supporting Information), the number of interatomic-polarized charges is not much altered by the concentration of Co atoms; meanwhile, the Pt atoms near the Co atom can accumulate more electrons to generate highly active sites in either neutral state or with the addition of extra electrons as mentioned above (depicted by Figure S5 in the Supporting Information). In this case, the increasing number of Co atoms in the lattices should
enhance the catalytic activity of Pt sites near the Co centers for the HER.

Besides the surface charges, surface electronic structure is another key parameter to electrocatalysis.\[^{[10]}\] To reveal the surface electronic structures, we further calculate the projected density of states (PDOS) of Pt d orbitals in the three models (Figure 4e and Figure S16 in the Supporting Information). As compared with bimetallic alloys (Pt\(_{61}\)Fe\(_{22}\)Co\(_{5}\), Pt\(_{61}\)Fe\(_{18}\)Co\(_{9}\), Pt\(_{61}\)Fe\(_{20}\)Co\(_{7}\), Figure S17 in the Supporting Information), the incorporation of Co into the PtFe lattice partially introduces some impurity states around the Fermi level as Co possesses one more d electron than Fe, indicating their d-orbital couplings.

More importantly, the PDOS distribution gradually shifts along with the increase of Co content. To better examine the electronic structures of the Pt d orbitals, we average the energy levels of all the d electrons in Pt atoms and acquire the values of d-band centers as listed in Table 2. The d-band center depicts the electrocatalytic activity of metals. It is known that most electrocatalytic reactions hold a volcano relationship between d-band center and the electrocatalytic activity of metals.\[^{[10]}\]

In other words, the d-band center too close to or far from the Fermi level would reduce the electrocatalytic activity of metals. In our case, the d-band center moves upward toward the Fermi level with the increase of Co:Fe ratio, and thus would make the medium atomic ratio (e.g., 7:20) the best for HER activity.\[^{[10]}\] Specifically for the HER reaction, the metal d-orbital electrons contribute to both metal-H bond formation and bond-breaking saddle point.\[^{[37–41]}\] For this reason, tuning the d-band center by composition engineering provides an approach to maneuvering the reaction process, leading to the improvement of HER performance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d-Band center, Pt PDOS (neutral) [eV]</th>
<th>d-Band center, Pt PDOS (1 e(^{-})) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spin up</td>
<td>Spin down</td>
</tr>
<tr>
<td>Pt(<em>{61})Fe(</em>{22})Co(_{5})</td>
<td>-4.54</td>
<td>-3.88</td>
</tr>
<tr>
<td>Pt(<em>{61})Fe(</em>{18})Co(_{9})</td>
<td>-4.33</td>
<td>-3.94</td>
</tr>
<tr>
<td>Pt(<em>{61})Fe(</em>{20})Co(_{7})</td>
<td>-4.26</td>
<td>-3.96</td>
</tr>
<tr>
<td>Pt(<em>{61})Fe(</em>{22})Co(_{5})</td>
<td>-4.22</td>
<td>-4.00</td>
</tr>
<tr>
<td>Pt(<em>{61})Co(</em>{27})</td>
<td>-4.23</td>
<td>-3.79</td>
</tr>
</tbody>
</table>

In summary, we have developed a synthetic approach to trimetallic PtFeCo alloy nanostructures with controllable compositions and in a unique TriStar shape. The HER performance of these TriStar nanostructures turns out to have a strong correlation with the chemical compositions, to which interatomic charge polarization and d electron couplings may both make contributions. In particular, the chemical composition is potentially the knob for altering the HER reaction process by maneuvering the d-band centers. The surface structure enabled by the TriStar shape further enhances the HER activity of samples by increasing the number of active sites and reducing the contact resistance. The PtFeCo TriStar 3 sample well combines the surface design with the composition engineering, achieving current density up to 1325 mA cm\(^{-2}\) at potential of -400 mV. This synergistic working mechanism, which reduces the usage of Pt and boosts HER performance by forming alloys, opens up new possibilities for designing low-cost, high-performance electrocatalysts. We envision that it would provide fresh insights into rationally designing the alloy electrocatalysts from a different perspective.

**Experimental Section**

**Nanostructure Synthesis:** The synthesis was carried out by employing a standard anion exchange procedure. The doses of chemical agents and reaction temperatures as listed in Table S2 (Supporting Information). In a typical procedure, 0.09 mmol of platinum (II) acetylacetonate (Pt(acac)\(_{2}\)), 0.36 mmol of iron (III) nitrate (Fe(NO\(_{3}\))\(_{3}\)), 0.01–0.045 mmol of cobalt (II) acetylacetonate (Co(acac)\(_{2}\)), 0.5 mmol of 1,2-tetradecanediol (TDD) and 0.05 mmol of tetracyclammonium bromide (TOAB) were mixed in 7.0 mL of 1-octadecene (ODE). The mixture was heated to 110 °C with vigorous stirring under the protection of Argon stream. 0.6–0.7 mL of oleic acid (OA), 1.3–1.4 mL of oleylamine (OLA) and 0.28 mL of the prepared 1-dodecanethiol (DDT) solution (0.08 mmol of DDT in ODE) were sequentially injected into the mixture. The color of the solution turned dark brown once all the chemicals were completely dissolved in the solvent, deeper dark with the increase of temperature, and finally black at around 180 °C. After a process at 215–222 °C for 30 min, 6.0 mL of toluene was injected to quench the reaction. These colloids were cooled down to room temperature by quickly removing the heating source, and then isolated by the addition of 40 mL hexanal and centrifugation. The dark yellow supernatant was then discarded. The precipitate was dispersed in 15 mL of hexane, and separated from the solution by the addition of 20 mL ethanol and centrifugation. The dispersion/pipetion procedure was repeated five times, and the final product was dispersed in hexane for further use.

**HER Measurements:** All the electrochemical measurements were performed in a three-electrode system on an electrochemical workstation (CHI 760E, Shanghai Chenhua, China) in 0.5 M H\(_{2}\)SO\(_{4}\) electrolyte. The catalysts dispersed onto a glassy carbon rotating disk electrode (GC RDE, PINE, PA, USA) was used as a working electrode, while a platinum foil and a reversible hydrogen electrode (RHE) served as the counter and reference electrodes, respectively. The GC RDE has a diameter of 5 mm and a geometric area of 0.19625 cm\(^2\). The electrode was first polished with emery paper of decreasing grades and then with Al\(_{2}\)O\(_{3}\) powders with size down to 0.05 μm. Prior to the deposition of catalysts, the electrode was immersed in ethanol and then thoroughly rinsed with DI water three times to remove contaminants. To prepare the working electrode, 0.01 g of nanoparticles were added to 10 mL of ethanol solution containing 0.4 g tetrabutylammonium hydroxide (TBAOH) and stirred at 25 °C for several days to remove the surfactants. The products were then separated via centrifugation, purified by three successive cycles of ultrasonic treatment and centrifugation with ethanol, and finally dispersed in ethanol aqueous solution (1:1, volume ratio) for electrochemical measurements. 20 µL of a suspension containing 0.01 mg catalysts was transferred to the GC RDE. Commercial Pt/C catalysts (E-TEK, Pt: 40 % wt., 0.01 mg Pt) were used as a reference to evaluate the electrocatalytic performance of various samples. Prior to electrocatalytic measurements, the working electrode was cleaned with RF plasma (Plasma Cleaner pdc-002, Harrick, NY, USA) at a power level of 10.5 W for 1.5 min to remove residue organics, and then covered with 10 µL of Nafion dispersed in water (0.05%). Hundreds of potential cycles were conducted in 0.5 M H\(_{2}\)SO\(_{4}\)(aq) solution with continuous Ar gas in the potential region from 0.05 to 1.05 V at a sweep rate of 50 mV s\(^{-1}\).
til the cyclic voltammetry curves (CVs) stay unchanged, in order to let residue organics and ions release. The XPS spectrum in Figure S18 (Supporting Information) shows that the samples after the cleaning are free of bromide (a component ion in the capping agent TOAB), indicating that such a cleaning procedure can effectively remove residue organics and ions from sample surface. Linear sweep voltammetry from 0.1 to −0.4 V with a scan rate of 2 mV s⁻¹ was performed with a flow of Ar gas maintained over the electrolyte during the HER experiment to eliminate dissolved oxygen. The working electrode at the electrolyte level was rotated at 1600 rpm to remove hydrogen gas bubbles formed at the catalyst surface. Cyclic voltammetry (CV) was carried out between −0.4 and 0.1 V versus RHE at 50 mV s⁻¹ for 5000 times to investigate the cycling stability. The iR corrections were employed when performing electrochemical characterizations, in order to reduce the negative impacts from the system resistance and adsorption processes.[43]

The blank CVs were collected in the potential region from 0.05 to 1.05 V at a sweep rate of 50 mV s⁻¹ in the freshly prepared 0.5 M H₂SO₄ solution. The EIS was carried out in the frequency range of 10⁻¹ to 10⁶ Hz with an AC voltage amplitude of 10 mV at a bias potential of −0.01 V versus RHE in 0.5 M H₂SO₄ solution.

**Computational Methods:** We have employed the Vienna ab initio Simulation package[27] to simulate the geometric and electronic properties of various model systems. Calculations were performed at the spin-polarized density functional theory level using the frozen-core and Perdew–Burke–Ernzerhof functions. An all-electron projector augmented wave model with the generalized gradient approximation and Perdew–Burke–Ernzerhof functions. An energy cutoff of 500 eV was used for the plane-wave expansion of the electronic wave function. The force and energy convergence criterion was set to 0.01 eV Å⁻¹ and 10⁻⁶ eV, respectively. Only Gamma point was performed for the first Brillouin zone. The structures in Figure S5a,b (Supporting Information) were a 3 × 3 × 3 supercell structure from the Pt₃Fe unit and the Pt₃Co unit, respectively. The structures in Figure S5c (Supporting Information) and Figure 4a–c were derived from the structure in Figure S5a (Supporting Information) with 1, 5, 7, and 9 Fe atoms replaced by Co (which were distributed as uniformly as possible), respectively. A Bader charge analysis was performed on all these systems.[43] The d-band centers were calculated using the spin-polarized d-orbital PDOS for Pt atoms.

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

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