Electrocatalysis



Enhancing Oxygen Evolution Reaction through Modulating Electronic Structure of Trimetallic Electrocatalysts Derived from Metal–Organic Frameworks

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The construction of efficient, durable, and non-noble metal electrocatalysts for oxygen evolution reaction (OER) is of great value but challenging. Herein, a facile method is developed to synthesize a series of trimetallic (W/Co/Fe) metal–organic frameworks (MOFs)-derived carbon nanoflakes (CNF) with various Fe content, and an Fe-dependent volcano-type plot can be drawn out for WCoFe_x-CNF. The optimized WCoFe_{0.3}-CNF (when the feed ratio of Fe/Co is 0.3) demonstrates superior electrocatalytic performance with a low overpotential of only 254 mV@10 mA cm⁻² and excellent durability of 100 h. Further researches show that appropriate amount of iron doping can regulate the electronic structure, resulting in a favorable synergistic environment. This method may stimulate the exploration of electrocatalysts by utilizing MOFs as precursors while realizing electronic modulation by multimetal doping.

1. Introduction

Nowadays, a large number of advanced technologies are closely dependent on traditional energy sources like coal, oil, and

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natural gas. However, these nonrenewable resources will eventually be exhausted. Therefore, searching alternative energy sources is extremely important with epochal significance.^[1] In developing more efficient electrochemical energy storage and energy conversion systems such as water electrolysis/photolysis, the fuel cells and the metal-air batteries, oxygen evolution reaction (OER) is deemed as a pivotal half-reaction.^[2] However, the breaking of O-H bond and the formation of O-O bond require high energy consumption, leading to sluggish kinetics. Therefore, OER peremptorily requires efficient electrocatalysts with excellent properties.^[3] Unfortunately, although RuO₂ and IrO₂

are the benchmark OER electrocatalysts at the current stage, their high price and scarcity have limited their widespread applications.^[4] Thus, searching efficient and low-cost catalysts is highly desirable.

Compounds based on the first row of transition metals (3d TMs, such as Fe, Co, and Ni) have been demonstrated to enhance the electronic occupancy status with improving the electron transfer ability. So, it is not surprising that they have been widely studied to replace precious metal-based electrocatalysts.^[5] Since it is well known that the interaction between various compositions in a multimetal structure can produce additional synergistic effects and leads to better electronic properties, forming a multimetallic structure is widely considered as a new strategy to design new electrocatalysts.^[6] Recently, it has been reported that the doping of foreign metal atoms (having similar electronic configuration of the metals in host matrix) into the crystal lattice can markedly improve the electronic structure of the host materials.^[7] Li et al. found that the right amount of iron doping can optimize the electronic structure of the active sites, resulting in the enhancement of catalytic performance.^[8] Comparing to 3d TMs, tungsten (W) has a higher electron-donating ability while being able to regulate the electronic structure of 3d energy bands, thereby optimizing the adsorption energies of OER intermediates.^[9] But, if the composition and electronic structure of the catalyst are not accurately regulated, the as-prepared multimetallic electrocatalysts still need a large overpotential to drive OER. In order to better construct the relationship between the component and the property among different electrocatalysts, metal-organic frameworks (MOFs) with



well-tunable chemical structures and morphologies have stimulated wide interest as emerging precursors and templates for carbon-based nanocomposites.^[10] For instance, Weng et al. proposed a MOF-derived ternary CoWP@C for efficient overall water splitting through a pyrolysis-phosphorization strategy.^[9a] He et al. designed bimetallic MOF-converted NiFe-based MILSP for oxygen-evolution catalysis.^[11] The merits of using multimetallic MOFs to obtain high-efficientcy electrocatalysts are as follows: First, different metals can be integrated into one single MOF without changing the original topology. Second, the catalytic properties can be promoted owing to the coupling effect among diverse metals. Third, different metal active sites may possess different functions. For example, Co can serve as electrocatalytic active sites while Fe can boost conductivity. Mn centers can adjust the intrinsic activities of the catalysts.^[12] However, hindered by the complicated synthetic processes and intricate synergetic effects, the research on trimetallic MOFderived catalysts is still at an initial stage.

In this work, we propose a facile strategy to obtain trimetallic electrocatalysts derived from hybrid zeolitic imidazolate frameworks (HZIFs) and a composition-activity volcano-type plot of WCoFe_x-CNF was developed. The electronic structure of the active sites can be facilely optimized by doping an appropriate amount of iron into the precursors, when the iron content is 30% of cobalt, the electrocatalytic property of WCoFe_{0.3}-CNF is located at the top of volcano, reaching only 254 mV at a current density of 10 mA cm⁻² with the Tafel slope of 44.8 mV dec⁻¹. In the meantime, WCoFe_{0.3}-CNF also exhibits extraordinary durability, which shows only slightly performance loss even after 5000 cycles and 100 h of continuous operation, outperforming most of the noble metal–free electrocatalysts reported so far.

2. Results and Discussion

2.1. Catalyst Synthesis and Characterization

The synthesis process of HZIFs-derived electrocatalysts is schematically illustrated in **Figure 1** (more details in the Experimental Section). In the framework of HZIF-W, a polyhedron formed by 3d transition metals and 2-methylimidazole is linked to WO₄²⁻ units, forming metal–organic zeolite under microwave condition^[13] and the HZIFs were used as templates to fabricate WCoFe_x-CNF through a controllable carbonization and oxidation process. The MOF precursors and obtained

electrocatalysts were denoted as WCoFe_x-MOF (WCo-MOF) and WCoFe_x-CNF (WCo-CNF) depending on the molar ratio of Fe/Co.

The scanning electron microscopy (SEM) images of the as-obtained MOF precursors were shown in Figure 2a,b and Figure S1 in the Supporting Information. HZIFs with different iron content have slight differences in morphologies. The higher the doping amount of Fe, the coarser the surface of the nanoflakes are. Figure 2a shows the SEM images of WCoFe0.3-MOF in low magnification and the surface of WCoFe0.3-MOF is relatively smooth. A shape of square nanoflakes can be observed and these nanoflakes have a lateral length of 200 nm and a thickness of 30 nm in average. After pyrolysis and oxidation process, the original morphology basically remained and the surface of the MOF flakes became uneven, rough and porous (Figure 2c; Figure S1g,h, Supporting Information). The size of WCoFe_{0.3}-CNF is similar to the WCoFe_{0.3}-MOF template. The transmission electron microscopy (TEM) images further confirm that WCoFe0,3-CNF is consisted of solid nanoparticles (Figure 2d). The continuous fringe lattices with a spacing of 0.29 nm can be indexed into the (-221) plane of CoWO₄ phase as shown in Figure 2e, which confirms the formation of metal oxides. Furthermore, the energy dispersive spectrometer (EDS) mappings showed that W, Co, Fe, and C are homogeneously distributed throughout the nanoflakes as shown in Figure 2f,j.

The X-ray diffraction (XRD) patterns of HZIFs template show sharp and distinct reflection in Figure S2 in the Supporting Information, which indicate that HZIFs were successfully synthesized with good crystallinity. The typical XRD patterns of HZIFs and WCoFe_x-CNF (WCo-CNF) are shown in Figure 3 and Figure S3 (Supporting Information). The patterns of WCo-CNF and WCoFe_x-CNF are well indexed into WC (PDF no.65-4539), which is corresponding to (001), (100), (101) planes at 31.6°, 35.7°, and 48.4° respectively. As for $WCoFe_x$ -CNF, different metal oxide/metal carbide nanoparticles can be indexed in the patterns. While changing the feeding ratio of MOF precursors, the diffraction peak patterns are approximately similar. The diffraction peaks at 18.7°, 23.8°, 24.4°, 31.3°, 41.2°, and 53.6° in the pattern of WCoFe_{0.3}-CNF can be assigned to the (100), (011), (110), (020), (-121), and (-221) planes of Co(Fe) WO₄, which means that iron was successfully doped into the original bimetallic electrocatalysts. It can be also observed that the diffraction peaks at 25.9° and 37.0° can be assigned into the (011) and (-211) planes of WO₃ respectively (PDF no.54-0508), which suggests the presence of high valance tungsten.



Figure 1. Schematic illustration of the synthesis of MOFs-derived electrocatalysts.







Figure 2. SEM images of WCoFe_{0.3}-MOF in a) low magnification and b) high magnification. c) SEM image and d,e) TEM images of WCoFe_{0.3}-CNF. f) Scanning TEM images of WCoFe_{0.3}-CNF and corresponding EDS elemental mapping images of g) W, h) Fe, i) Co, and j) C for WCoFe_{0.3}-CNF.

X-ray photoelectron spectroscopy (XPS) was carried out to reveal the valence and chemical environment of surface elements as shown in **Figure 4** and Figures S4 and S5 (Supporting Information). The Co 2p spectrum exhibits the existence of Co^{2+} and Co^{3+} . The $2p_{1/2}$ peak can be deconvoluted to Co^{2+} and Co^{3+} at 798.1 and 796.6 eV and the fitting peaks at 782.4 and 780.7 eV represent the $Co^{2+} 2p_{3/2}$ and $Co^{3+} 2p_{3/2}$, together with two satellite peaks at 786.3 and 803.0 eV (Figure 4a).^[14] As shown in Figure 4b, two binding energy peaks can be allocated to Fe $2p_{1/2}$ and Fe $2p_{3/2}$, together with a satellite peak at 716.1 eV. After



Figure 3. XRD patterns of WCo-CNF, WCoFe_{0.2}-CNF, and WCoFe_{0.3}-CNF.

deconvolution, the peaks located at 710.4 and 724.0 eV were attributed to Fe²⁺ and the peaks centered at 711.8 and 725.4 eV were assigned to Fe3+.[15] Inspection of the W 4f spectrum (Figure 4c) showed strong signals at 35.2 and 37.2 eV, which confirms the existence of WO₃.^[16] The spectrum of C 1s can be divided into three peaks centered at 287.7, 284.5, and 284.1 eV, suggesting the existence of C=O, W-C, and C=O respectively, which further confirmed the formation of tungsten carbide (Figure 4d).^[17] The deconvolution of the spectrum of O 1s revealed the coexistence of carbon-oxygen bond (532.6 eV, O3), oxygen vacancy (530.7 eV, O2) and metal-oxygen bond (530.1 eV, O1) as shown in Figure S4c in the Supporting Information.^[18] Three major peaks observed for N at 401.1, 400.0, and 398.3 eV can be assigned to graphitic N, pyrrolic N and pyridinic N (Figure S4b, Supporting Information).^[19] The quantitative analyses of element content calculated by XPS is shown in Table S1 in the Supporting Information.

2.2. OER Electrocatalytic Performance

The OER electrocatalytic performance of the MOFs-derived catalysts were evaluated in a typical three-electrode system in room temperature. The samples on the Nickle foam electrode were investigated in 1 \times KOH with a loading of 1.6 mg cm⁻². **Figure 5**a shows the OER polarization curves of WCoFe_x-CNF, WCo-CNF, and commercial IrO₂ versus reversible hydrogen electrode (RHE). All of the polarization curves were conducted without iR compensation. In Figure 5a, the bimetallic WCo-CNF showed the worst catalytic performance with the overpotential







Figure 4. High resolution a) Co 2p, b)Fe 2p, c) W 4f, and d) C 1s XPS spectra of WCoFe0.3-CNF.

of 325 mV at 10 mA cm⁻². The overpotential at 10 mA cm⁻² gradually reduced to 282 and 273 mV for WCoFe_{0.1}-CNF and WCoFe_{0.2}-CNF, and the optimized WCoFe_{0.3}-CNF could reach a very low overpotential (254 mV), which is 55 mV smaller than that of the commercial IrO2 (309 mV) and the majority of the previously reported cobalt-based OER electrocatalysts (Table S2, Supporting Information). It has been reported that doping an appropriate amount of a foreign metal atom with a similar electronic configuration into the original crystalline lattice can markedly optimize the electronic structure of the active sites, thereby significantly increasing the electrocatalytic activity of transition metal-based electrocatalysts.^[7a] However, when the feed proportion of Fe/Co continued to rise, there occurred a degradation of electrocatalytic performance which may be caused by the excessive doping of iron. In this way, we can clearly draw a Fe-reliant volcano-type plot as shown in Figure 5e. Moreover, polarization curves were also conducted using glass carbon (GC) as electrode and the trend of OER performance remains unchanged (Figure S6, Supporting Information). The double layer capacitance (C_{dl}) is calculated to represent the electrochemical active surface area (ECSA) by cyclic voltammogram (CV) as shown in Figure S7 in the Supporting Information. The C_{dl} for WCo-CNF, WCoFe_{0.1}-CNF, WCoFe_{0.3}-CNF and WCoFe_{0.6}-CNF is 1.44, 3.40, 5.72, and 0.60 mF cm⁻², the WCoFe_{0.3}-CNF presented largest C_{dl} value, resulting in abundant exposed active sites for OER. The OER kinetic mechanism was studied via the Tafel plots as shown in Figure 5b and the Tafel values for WCo-CNF, WCoFe_{0.2}-CNF,

WCoFe_{0.3}-CNF, WCoFe_{0.4}-CNF and commercial IrO₂ are 59.9, 50.6, 44.8, 48.0, and 50.1 mV dec⁻¹, respectively. Obviously, the WCoFe_{0.3}-CNF displayed best OER kinetics among the trimetallic MOFs-derived electrocatalysts. These results demonstrate that an appropriate amount of foreign atom doping can induce better kinetics. In addition, Electrochemical Impedance Spectroscopy (EIS) was conducted to evaluate the interfacial electron/proton transfer activity of the electrocatalysts.^[20] The EIS Nyquist plots are shown in Figure S8 in the Supporting Information, and the R_{ct} for WCo-CNF, WCoFe_{0.3}-CNF and WCoFe_{0.6}-CNF is 55, 36, and 95 Ω respectively. WCoFe_{0.3}-CNF exhibited the smallest charge transfer resistance (R_{ct}) , which indicated a higher charge transfer capability. It can be obviously observed that the semicircle of trimetallic WCoFe_{0.6}-CNF is much bigger than that of WCo-CNF. The overdoping of iron increases the charge transfer resistance, thereby decreasing the electrocatalytic performance.

Durability is an important factor in practical applications, and chronopotentiometric strategy is conducted to investigate the durability of the optimized WCoFe_{0.3}-CNF (Figure 5c). After 100 h of continuous working at 20 mA cm⁻², 98.3% of the initial potential retained, which is superior to most of the reported electrocatalysts as shown in Table S2 in the Supporting Information. Moreover, the stability of WCoFe_{0.3}-CNF has been compared to noble metal catalyst RuO₂ as exhibited in Figure S9 in the Supporting Information, and the operating voltage of RuO₂ increased obviously within 8 h. The SEM image of and XRD pattern of WCoFe_{0.3}-CNF after 100 h of continuous



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Figure 5. a) OER polarization curves of WCoFe_x-CNF, WCo-CNF, and commercial IrO₂ in 1 \bowtie KOH solution. Scan rate: 5 mV s⁻¹, b) Tafel plots of WCoFe_x-CNF, WCo-CNF, and commercial IrO₂ in 1 \bowtie KOH solution for OER, c) the chronopotentiometric measurements of WCoFe_{0.3}-CNF for 100 h, d) the multistep chronopotentiometric curves for WCoFe_{0.3}-CNF; the inset in (d) shows polarization curves of WCoFe_{0.3}-CNF before and after 5000 cycles. e) A volcano-type plot of overpotential at 10 mA cm⁻² and f) a volcano-like change of the molar ratio of Co³⁺/Co²⁺.

operation is shown in Figure S10 in the Supporting Information. It can be observed that the morphology and structure of WCoFe_{0.3}-CNF maintained basically, indicating the ultra-high stability of WCoFe_{0.3}-CNF. Meanwhile, the OER capability of WCoFe_{0.3}-CNF working at different current densities was also tested. As shown in Figure 5d, when the current density was gradually increasing from 10 to 150 mA cm⁻², the overpotential of the WCoFe_{0.3}-CNF electrode increased and stabilized rapidly. Additionally, the trimetallic WCoFe_{0.3}-CNF is capable of working continuously and stably at a high current density. Moreover, the polarization curves of WCoFe_{0.3}-CNF after 5000 CV cycles almost overlapped with the initial one (inset in Figure 5d).

To further understand how foreign atom (Fe) doping enhances the intrinsic performance by electronic-modulation, we compared the Co 2p XPS spectrum of WCo-CNF and WCoFe_x-CNF (Figure S11, Supporting Information). It can be calculated that the molar ratio of Co^{3+}/Co^{2+} is 1.38 for WCoFe_{0.3}-CNF, 0.89 for WCoFe_{0.2}-CNF, and 0.85 for WCo-CNF, which indicates that suitable amount of Fe doping increased the oxidation state of Co. Although it has been confirmed in the previous literature that Co^{3+} has better electrocatalytic activity than $Co^{2+},^{[9b,21]}$ as the iron content continued to rise, the crystal structure of the HZIF precursors may be destroyed, thus causing the loss of Co^{3+} active sites.^[22] The same conclusion can be drawn in XPS spectrum of Co 2p. As shown in Figure S8 in the Supporting Information, the molar ratio of Co^{3+}/Co^{2+} for WCoFe_{0.4}-CNF, WCoFe_{0.5}-CNF and WCoFe_{0.6}-CNF gradually decreased. In this way, a composition-activity as well as Co^{3+}/Co^{2+} ratio volcano-type plot can be drawn. As shown in Figure 5e,f, with a right feeding amount of Fe, the optimized electronic structure of trimetallic WCoFe_{0.3}-CNF was proven to be the key factor in improving the OER catalytic performance.

3. Conclusion

To summarize, we innovatively developed a MOF-converted WCoFe trimetallic electrocatalyst for OER and a compositionactivity volcano-type plot has been revealed. The electronic structure of trimetallic carbon electrocatalysts can be modified by doping an appropriate amount of Fe, and the as-optimized WCoFe_{0.3}-CNF can be used as an efficient OER electrocatalyst with a low overpotential of 254 mV at 10 mA cm⁻² and a Tafel slope of 44.8 mV dec⁻¹, outperforming novel metal-based IrO₂ electrocatalysts. It also exhibited high durability with negligible activity degradation after 100 h of continuous working. Moreover, tungsten with a high electron-donating ability can further regulate the electronic structure of cobalt and iron, therefore boosting OER performance. The synergistic effects of electronic structural regulation have been proven to be the key to improve electrocatalytic performance. The novel strategy of studying the composition-activity relationship using MOFs as precursors may stimulate the exploration of electrocatalysts for various applications.

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Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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